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Buchanan et al.

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[54] **REMOVING SO_X, NO_X AND CO FROM FLUE GASES**

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[21] Appl. No.: **435,914**

[22] Filed: **May 5, 1995**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 184,536, Jan. 21, 1994, which is a continuation-in-part of Ser. No. 63,473, May 19, 1993, abandoned, which is a continuation of Ser. No. 868,432, Apr. 15, 1992, Pat. No. 5,229,091.

[51] **Int. Cl.**^{6} **B01D 53/46**; B01D 53/81; B01D 53/96

[52] **U.S. Cl.** **423/210**; 423/235; 423/244.02; 423/244.09; 423/246; 95/137; 588/205

[58] **Field of Search** 95/137; 96/131; 423/210, 222, 235, 244.02, 244.07, 244.09, 246; 588/205, 206, 207

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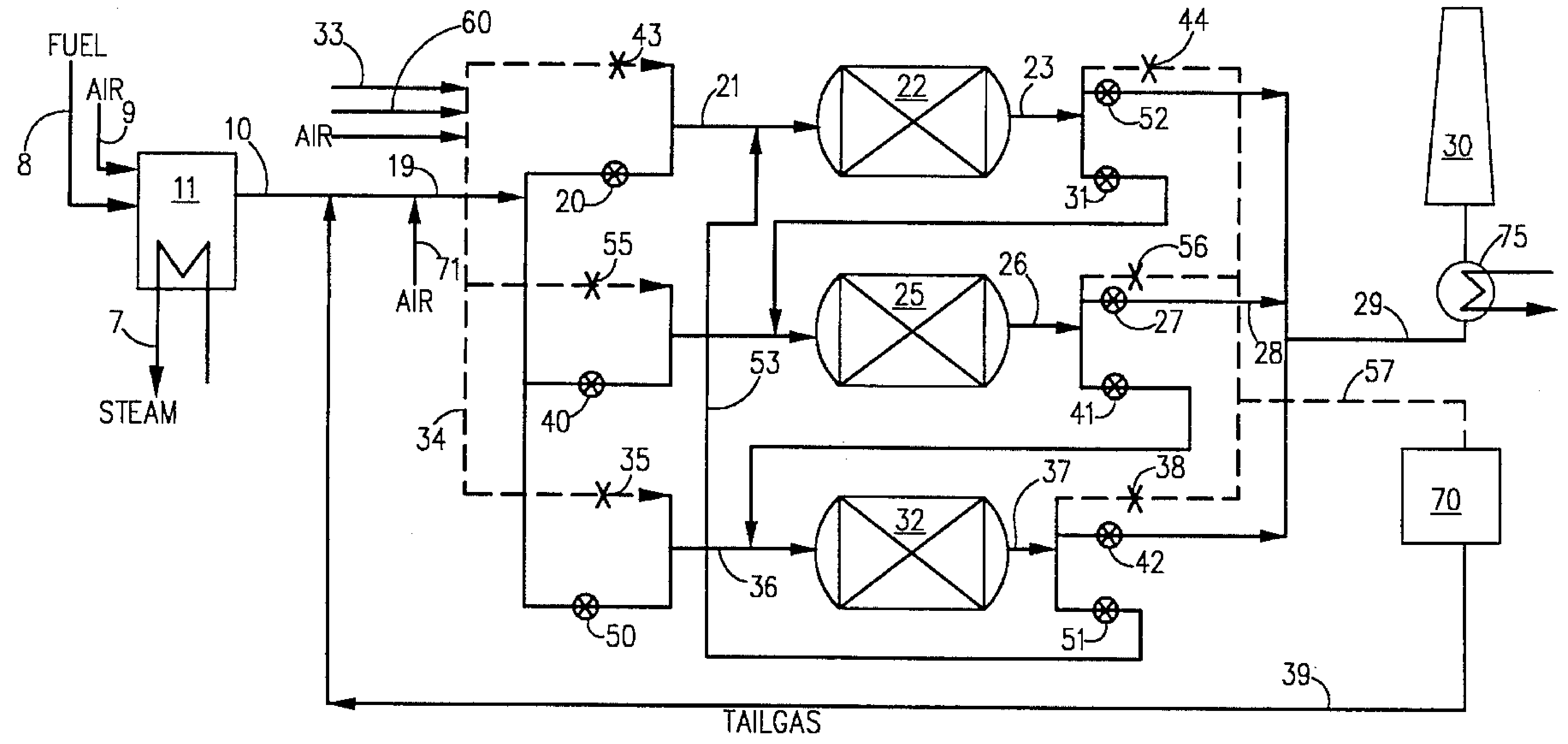
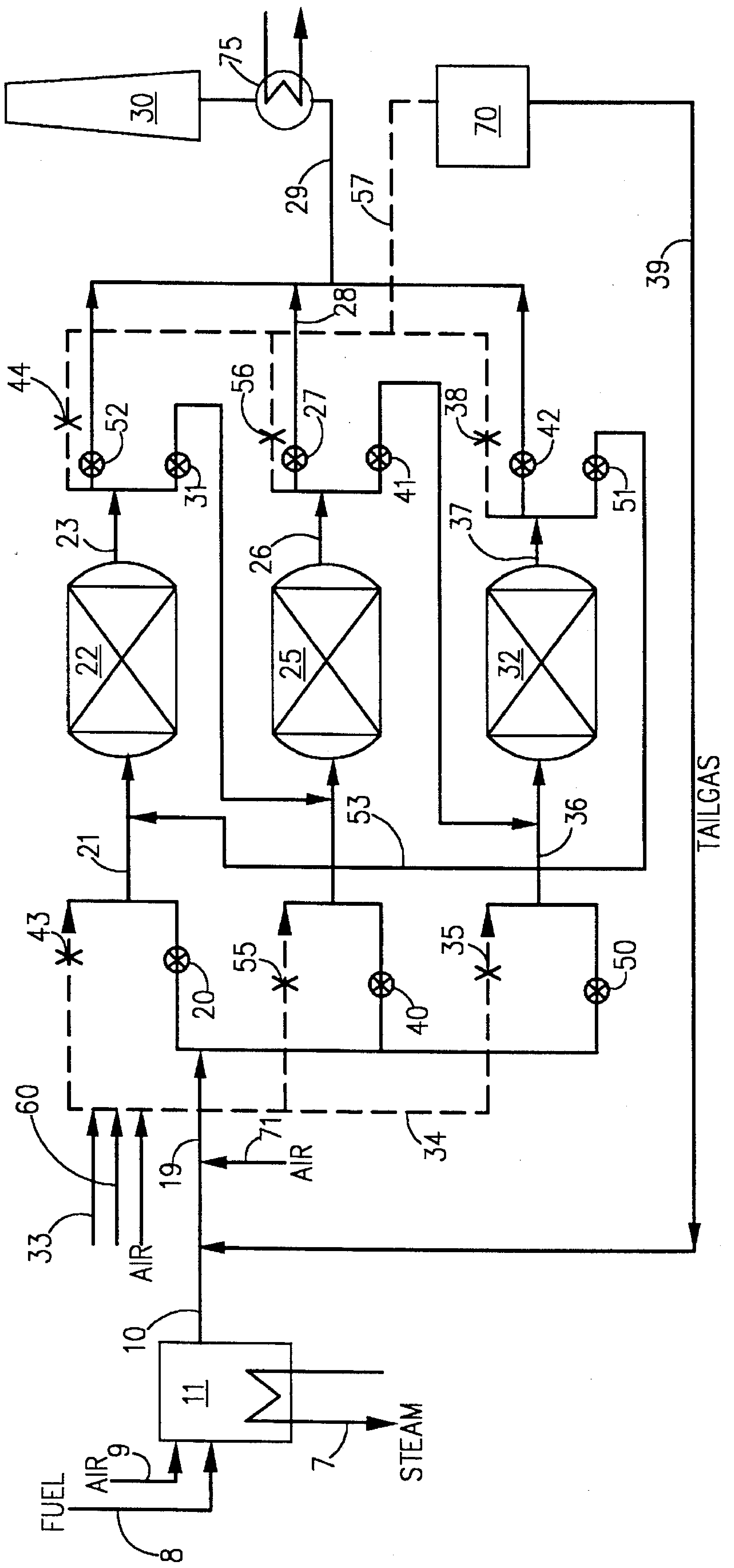
[57] **ABSTRACT**

Removing sulfur oxide and carbon monoxide in a flue gas stream by combusting fuel in the combustor with a reduced amount of oxygen to partially convert carbon monoxide therein to carbon dioxide and sufficient to convert all sulfur-containing species in the flue gas stream to sulfur oxide and thus form a sulfur oxide enriched gas stream having between at least about 500 ppm carbon monoxide. The sulfur oxide enriched gas stream is contacted with a solid adsorbent bed for adsorbing the sulfur oxides in the form of inorganic sulfates and/or sulfur oxides. The solid adsorbent contains a catalytic oxidation promoter for oxidizing the carbon monoxide gas stream to carbon dioxide, thus forming a sulfur oxide and carbon monoxide depleted stream for disposal. The adsorbent bed is then contacted with a reducing gas stream for regenerating the adsorbent bed to form a hydrogen sulfide and/or sulfur dioxide bearing stream.

25 Claims, 6 Drawing Sheets

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STEAM

FIG. 1

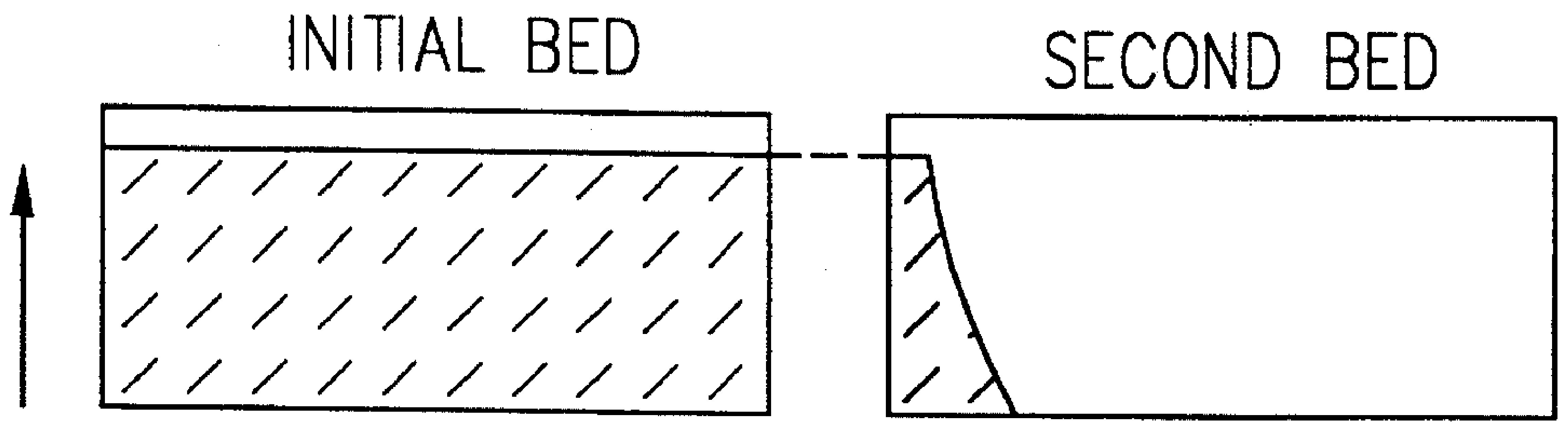

FIG. 2

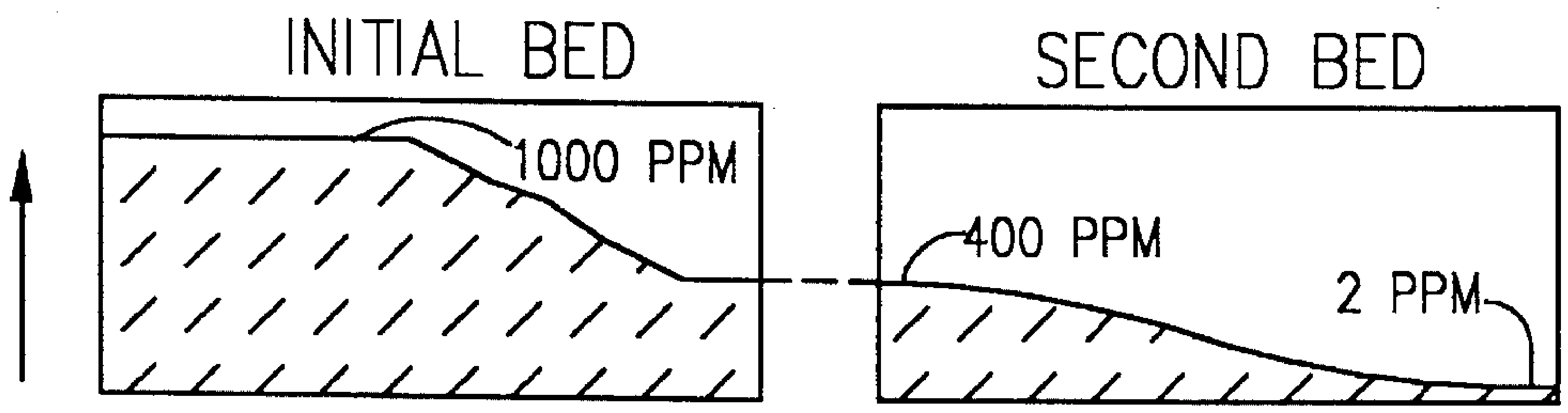

FIG. 3

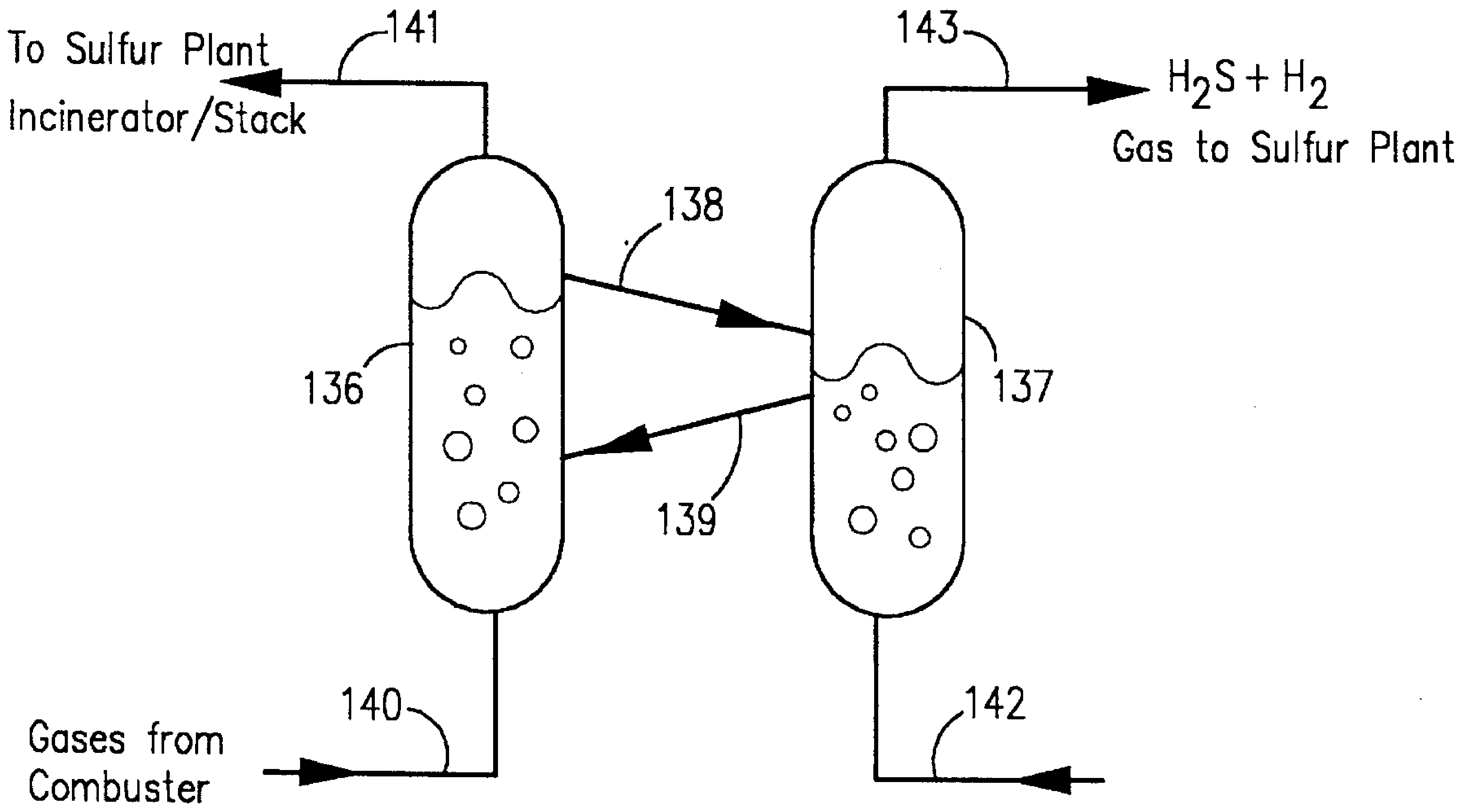

FIG. 4

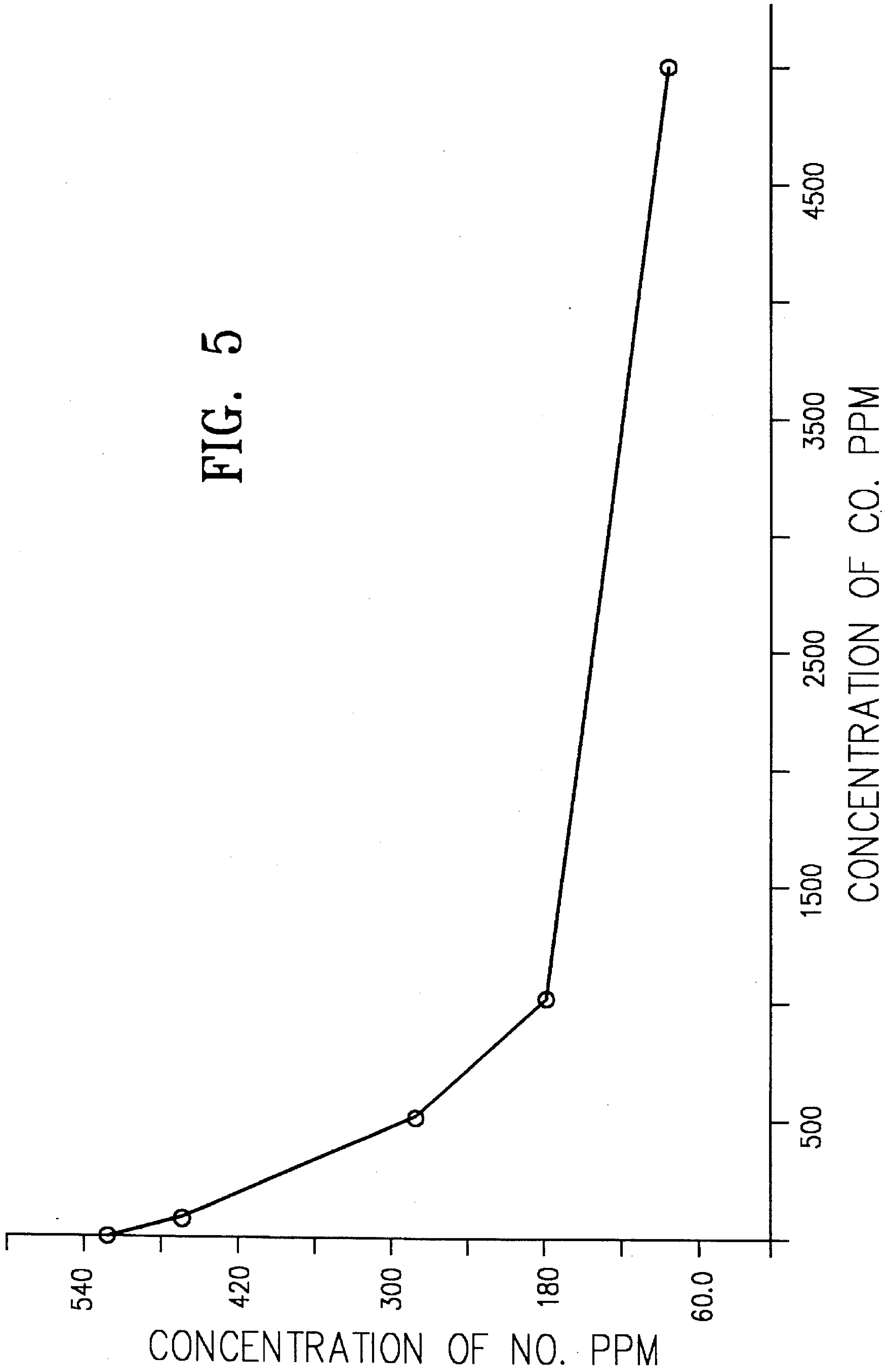

FIG. 5

CONCENTRATION OF CO. PPM
500
1500
2500
3500
4500
CONCENTRATION OF NO. PPM
540
420
300
180
60.0

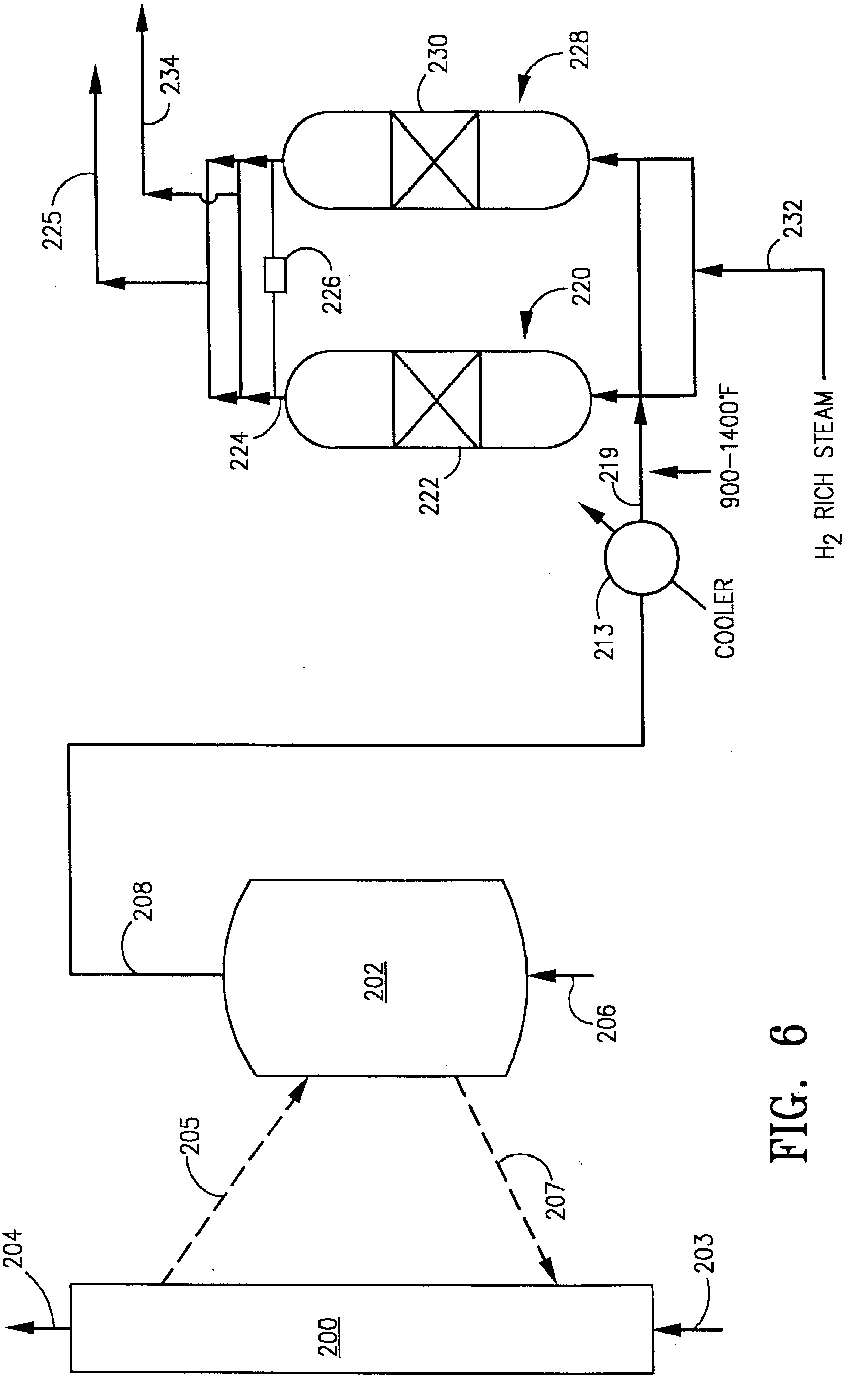
234
225
230
228
226
220
232
224
222
219
900–1400°F
H_2 RICH STEAM
213
COOLER
208
202
206
205
207
204
203
200

FIG. 6

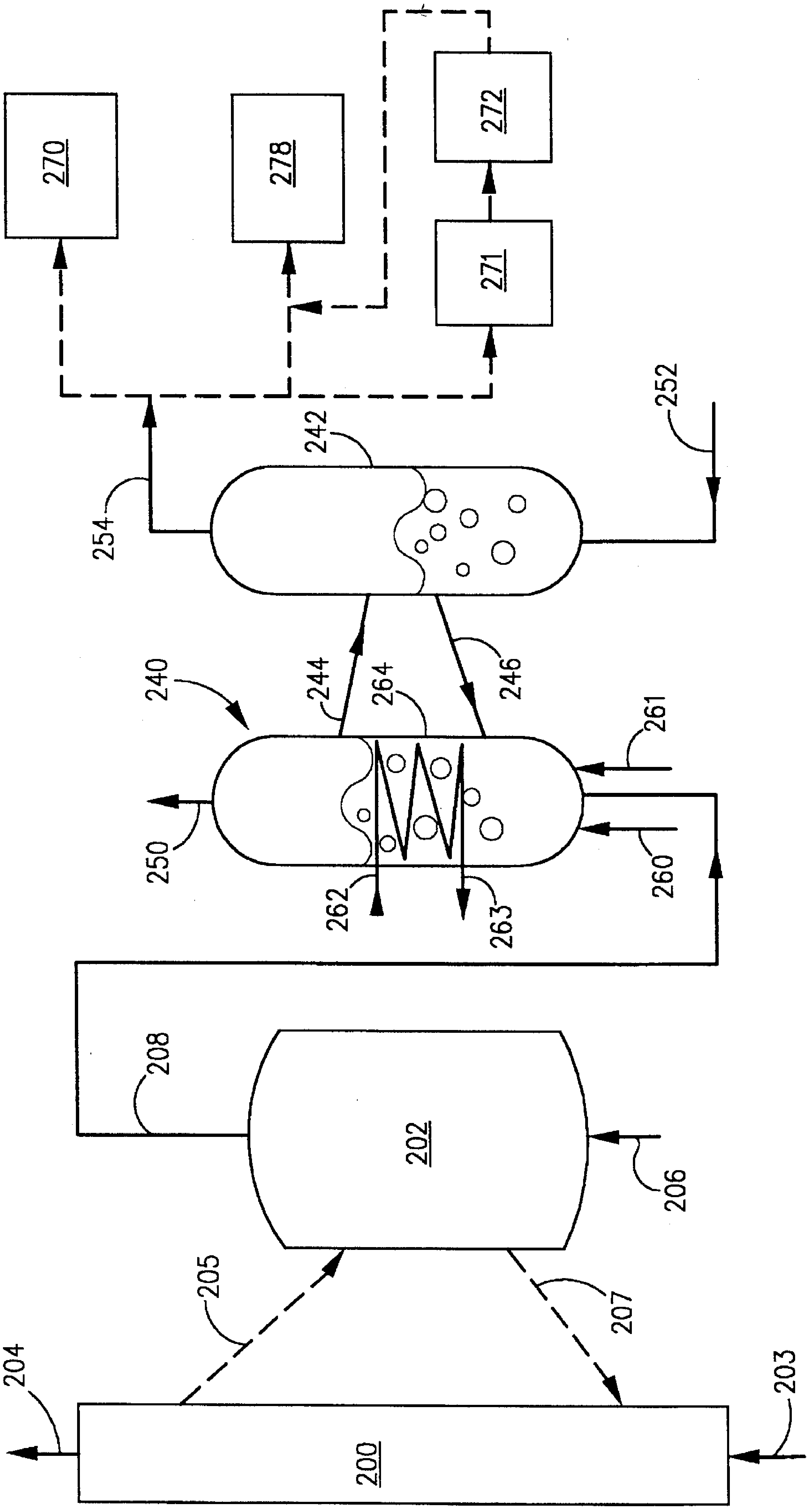
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FIG. 7

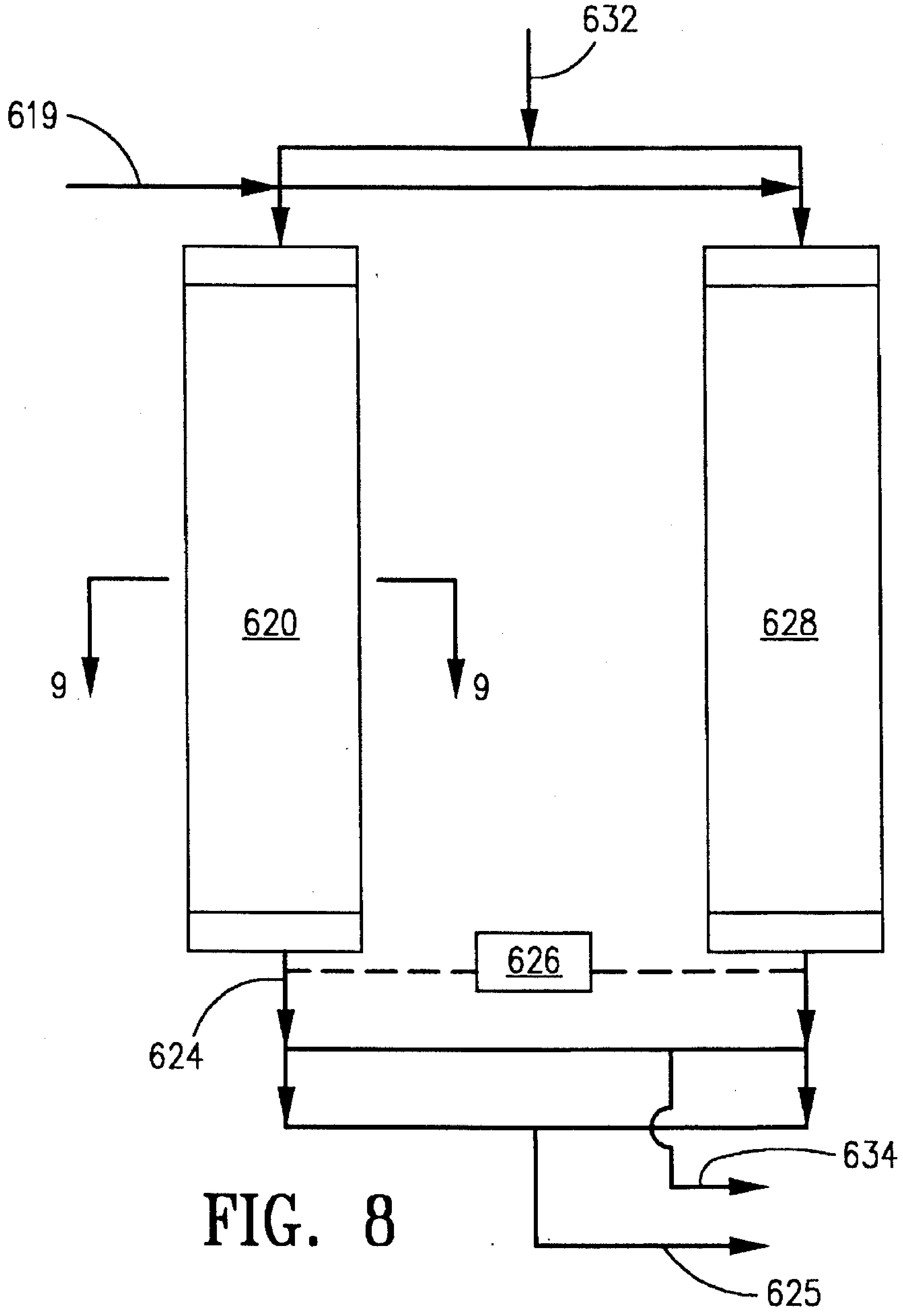

FIG. 8

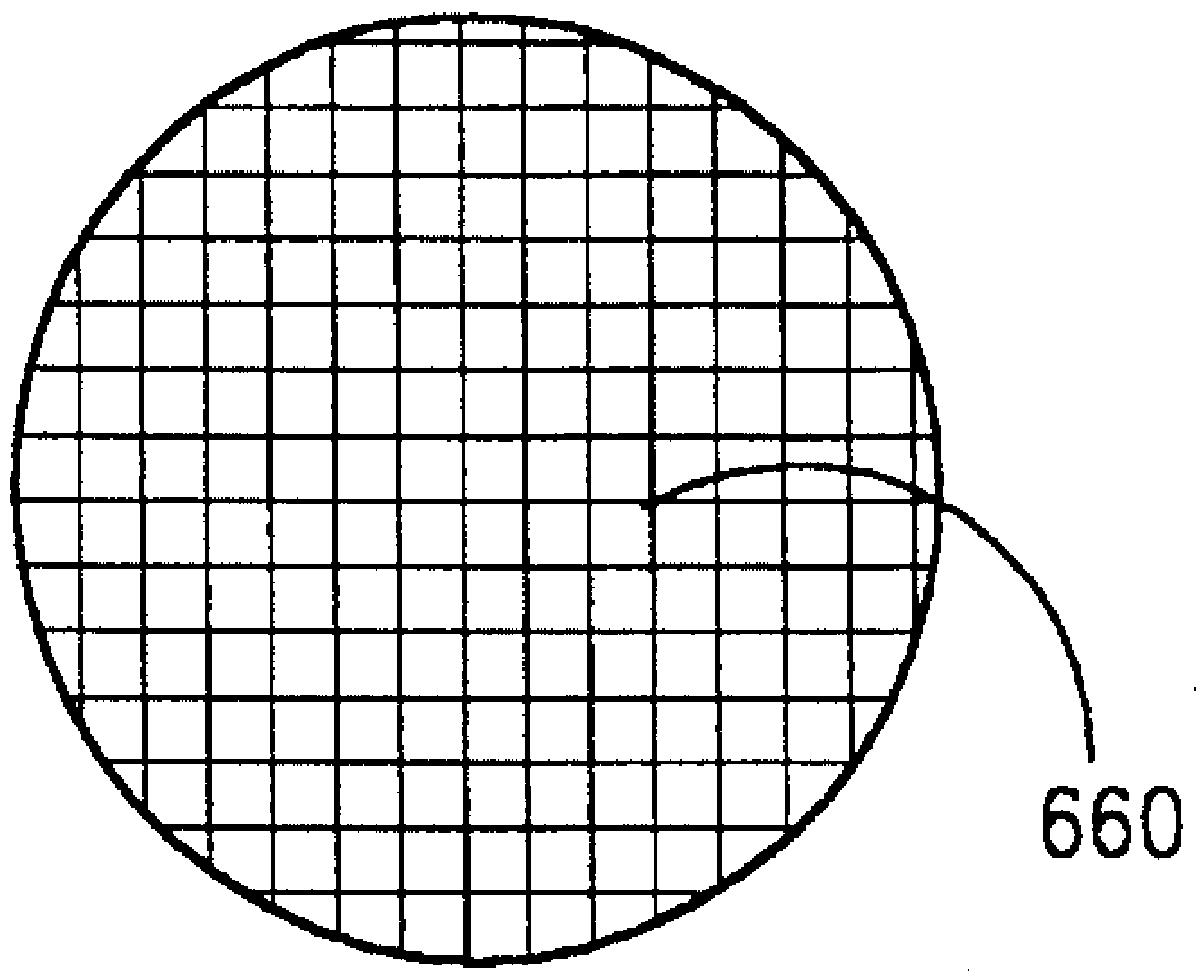

FIG. 9

REMOVING SO_X, NO_X AND CO FROM FLUE GASES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of application Ser. No. 08/184,536, filed Jan. 21, 1994, which is a continuation-in-part of application Ser. No. 08/063,473, filed May 19, 1993 now abandoned, which is a continuation of application Ser. No. 07/868,432, filed Apr. 15, 1992, and now U.S. Pat. No. 5,229,091.

BACKGROUND OF THE INVENTION

The present invention relates to a process and a system for removing sulfur oxide and carbon monoxide from a gas stream. More particularly, the present invention relates to a process and system for the removal of sulfur oxide and carbon monoxide from a flue gas stream with an oxidation step using a reduced amount of combustion air.

Combustor flue gas streams are typically desulfurized by injection of reactive solids such as lime or limestone, or by scrubbing in an alkaline aqueous solution. These treatments have varying degrees of effectiveness in removing SOx and do little to reduce NOx. The amount of air fed to combustors is usually maintained at greater than 110% of the stoichiometric requirement for complete combustion of fuels containing hydrogen and carbon to water and carbon dioxide. One reason for this amount of excess air is to ensure complete combustion of carbon monoxide to carbon dioxide.

SUMMARY OF THE INVENTION

In accordance with a broad aspect of the invention, there is provided a method of removing sulfur oxide and carbon monoxide in a flue gas stream from a combustor. By way of example, the combustor can be a unit using fuel and an oxygen-containing gas to generate a desired energy, or a regenerator of a fluid catalytic cracking unit and the like. The method comprises the steps of operating the combustor with a reduced amount of oxygen-containing gas to partially convert carbon monoxide therein to carbon dioxide, but with a sufficient amount of oxygen-containing gas to convert all sulfur-containing species in the flue gas stream to sulfur oxide and thus form a sulfur oxide enriched gas stream having at least about 500 ppm carbon monoxide. Then the sulfur oxide enriched gas stream is contacted with a solid adsorbent bed for adsorbing thereon the sulfur oxides in the form of inorganic sulfates or sulfur oxides or combinations thereof, the solid adsorbent containing a catalytic oxidation promoter for oxidizing the carbon monoxide in the sulfur oxide enriched gas stream to carbon dioxide, thus forming a sulfur oxide and carbon monoxide depleted stream for disposal. Thereafter the adsorbent bed is contacted with a reducing gas stream for regenerating the adsorbent bed by reducing the retained inorganic sulfates or sulfur oxides or combinations thereof to hydrogen sulfide and/or sulfur dioxide, and thereby forming a hydrogen sulfide and/or sulfur dioxide bearing stream which may be processed to remove the sulfur.

In accordance with another broad aspect of the invention, there is provided a method of removing sulfur oxide, carbon monoxide and nitrogen oxide in a flue gas stream from a combustor using fuel and an oxygen-containing gas to generate a desired energy. The method comprises the steps of combusting the fuel in the combustor with a reduced amount of oxygen-containing gas to convert all sulfur-containing species in the flue gas stream to sulfur oxide, and to partially convert carbon monoxide therein to carbon dioxide, thus forming a sulfur oxide enriched gas stream having at least about 500 ppm carbon monoxide and a consequential reduced amount of nitrogen oxide, the amount of nitrogen oxide in the sulfur oxide enriched gas stream being an inverse function of the amount of carbon monoxide therein.

Then the sulfur oxide enriched gas stream is contacted with a solid adsorbent bed for adsorbing thereon the sulfur oxides in the form of inorganic sulfates or sulfur oxides or combinations thereof, the solid adsorbent containing a catalytic oxidation promoter for oxidizing the carbon monoxide in the sulfur oxide enriched gas stream to carbon dioxide, thus forming a sulfur oxide and carbon monoxide depleted stream with the consequential reduced amount of nitrogen oxide for disposal. Thereafter the adsorbent bed is contacted with a reducing gas stream for regenerating the adsorbent bed by reducing the retained inorganic sulfates or sulfur oxides or combinations thereof to hydrogen sulfide and/or sulfur dioxide, and thereby forming a hydrogen sulfide and/or sulfur dioxide bearing stream.

In accordance with a specific aspect of the invention, the method further comprises recovering sulfur from the hydrogen sulfide and/or sulfur dioxide bearing stream.

In accordance with another broad aspect of the invention, there is provided a system for removing sulfur oxide, carbon monoxide and nitrogen oxide in a flue gas stream from a combustor using fuel and an oxygen-containing gas to generate a desired energy. The system comprises means for combusting the fuel in the combustor with a reduced amount of oxygen-containing gas to convert all sulfur-containing species in the flue gas stream to sulfur oxide, and to partially convert carbon monoxide therein to carbon dioxide, thus forming a sulfur oxide enriched gas stream having at least about 500 ppm carbon monoxide and a consequential reduced amount of nitrogen oxide, the amount of nitrogen oxide in the sulfur oxide enriched gas stream being an inverse function of the amount of carbon monoxide therein. Means are included for contacting the sulfur oxide enriched gas stream with a solid adsorbent bed for adsorbing thereon the sulfur oxides in the form of inorganic sulfates or sulfur oxides or combinations thereof. The solid adsorbent has a catalytic oxidation promoter for oxidizing the carbon monoxide in the sulfur oxide enriched gas stream to carbon dioxide, thus forming a sulfur oxide and carbon monoxide depleted stream with the consequential reduced amount of nitrogen oxide for disposal. Means are provided for contacting the adsorbent bed with a reducing gas stream for regenerating the adsorbent bed by reducing the retained inorganic sulfates or sulfur oxides or combinations thereof to hydrogen sulfide and/or sulfur dioxide, and thereby forming a hydrogen sulfide and/or sulfur dioxide bearing stream.

In another specific aspect, there is provided means for recovering sulfur from the hydrogen sulfide and/or sulfur dioxide bearing stream.

In accordance with yet another aspect of the present invention, there is provided a system for desulfurizing a gas stream including sulfur oxides comprising an elongated monolith, which includes an inlet end, an outlet end and a plurality of longitudinally extending honeycombed structures. The honeycombed structures have solid absorbent on the inner surfaces thereof or are formed at least in part of solid absorbent.

Thus, the invention relates to removing sulfur oxide and carbon monoxide from a gas stream such as a flue gas resulting from the combustion or oxidation of a fuel which contains sulfur. By combusting the flue gas with a reduced amount of air, such that all sulfur compounds are converted to sulfur oxide, but only part of carbon monoxide is converted to carbon dioxide, there is an unexpected reduction in nitrogen oxide in the output from the combustor. The flue gas from the combustor is contacted with a regenerable solid sulfur oxide sorbent which contains a catalytic oxidation promoter for oxidizing the carbon monoxide. Preferred solid sorbents contain magnesium and aluminum oxides. The sorbents are regenerated by contact with a reducing gas, which causes the sulfur to be desorbed, mainly as SO_2 and H_2S in a concentrated stream for recovery. Suitable reducing gases are hydrogen and/or hydrocarbons; or syngas (carbon monoxide and hydrogen).

Another aspect of the present invention relates to removing SOx from fluegas of the regenerator of a fluid catalytic cracking unit (FCC) by contacting the fluegas with a bed of solid sorbent. The sorbent is regenerated by contacting it with a reducing gas. The regenerated off-gas, containing H_2S and/or SO_2, is fed to an appropriate recovery unit. In this aspect, the FCC regenerator is run in a partial CO combustion mode, and the remaining CO combustion takes place catalytically in a SOx sorbent bed, which is preferably a fluid bed.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** is a schematic flow diagram of a three-bed system for recovering sulfur in accordance with the present invention from a gas stream including sulfur oxide and carbon monoxide;

FIG. **2** is a graphic representation of a steep adsorption front case wherein the first serially connected bed is almost totally utilized before frontal break-through;

FIG. **3** is a graphic representation of a shallow adsorption front case wherein the beds are preferably switched before saturation of the first bed, and before frontal break-through of the second bed;

FIG. **4** is a schematic flow diagram of a fluidized bed system for recovering sulfur in accordance with another embodiment of the present invention;

FIG. **5** is a graph relating the concentrations of CO to NO in the effluent of a fluid bed combustor;

FIG. **6** is a schematic flow diagram of a fixed-bed system for recovering sulfur and CO from an FCC flue gas stream in accordance with the present invention;

FIG. **7** is a schematic flow diagram of a fluidized bed system for recovering sulfur in accordance with another FCC embodiment of the present invention;

FIG. **8** is a schematic of a desulfurizing embodiment of the present invention including a monolith; and

FIG. **9** is cross-section of a monolith taken along line IX—IX of FIG. **8**.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The present invention provides for removing sulfur oxide and carbon monoxide from a flue gas resulting from combustion or oxidation of a fuel which contains sulfur, by contacting the flue gas with a regenerable solid sulfur oxide sorbent which contains a catalytic oxidation promoter. The promoter oxidizes carbon monoxide to carbon dioxide. Preferred solid sorbents contain magnesium and aluminum oxides. The sorbent is regenerated by contact with a reducing gas, which causes the sulfur to be desorbed, mainly as SO_2 and/or H_2S in a concentrated stream for recovery. Sulfur may be recovered, in for example a Claus plant, from said hydrogen sulfide and/or sulfur dioxide bearing stream, or the stream may be fed to an amine scrubber.

The ability of the sorbent to oxidize carbon monoxide permits a reduction in the amount of combustion air and also a reduction in combustion temperature. Reduction of the amount of combustion air has a number of advantages, among them being an improvement in fuel efficiency and a reduction in the amount of nitrogen oxide formed in the combustor.

The amount of combustion air is reduced, from the prior art requirement of greater than 110%, to from about 95% to about 110% of a stoichiometric amount of air or oxygen to convert all carbon monoxide in the gas stream to carbon dioxide.

The reduced amount of air or oxygen supplied to the combustor is selected to maintain the concentration of carbon monoxide in the sulfur oxide enriched gas stream at greater than 500 ppm, and preferably between about 600 ppm and 5,000 ppm. The amount of nitrogen oxide in the sulfur oxide enriched stream is an inverse function of the amount of carbon monoxide therein. The reason there usually is a need for an amount of air in excess of the stoichiometric amount, and still maintain the quantity of carbon monoxide in excess of 500 ppm is due to the inefficiency of combustor to effectively use oxygen to completely combust the fuel.

The preferred sorbent is a mixed oxide of magnesium and aluminum, with suitable oxidation promoters, which has a sulfur oxide uptake capacity of about 50 wt. %. Further, the contemplated system has demonstrated removal of SO_2 to below 1 ppm in the effluent to the stack. Finally, there is demonstrated the ability during sorbent regeneration to produce a concentrated stream of SO_2 and/or H_2S, suitable for further processing, for example in a Claus sulfur plant.

The preferred operating temperature for this process is about 1,200° F. for both adsorption of SOx and for regeneration of the sorbent. The sorbent is regenerated by contacting it with a reducing gas, such as hydrogen or light hydrocarbons or syngas (hydrogen and carbon monoxide). Sulfur is desorbed mainly as SO_2 and H_2S. Experiments have demonstrated that hydrogen promotes the formation of SO_2, while hydrocarbons can promote formation of either H_2S or SO_2, depending on operating conditions. In general, lower regeneration temperatures and higher hydrocarbon flow rates favor production of H_2S. The H_2S/SO_2 ratio can be further adjusted within the sulfur recovery unit by additional air or reducing gas, to obtain the optimal H_2S/SO_2 ratio for that process. For the Claus sulfur recovery process, an H_2S/SO_2 ratio of about 2 is desired.

Combustion flue gases usually contain appreciable amounts of fine particulates, which can plug the interstices between the granules in a conventional fixed bed. Forming the solid sorbent into monoliths with unobstructed passages will mitigate this problem, and will reduce pressure drop through the bed.

However, with a moving bed, the sorbent is circulated between adsorption and regeneration vessels. A moving bed can have a number of advantages in a flue gas application. For example the moving bed will be less subject to adverse effects of particulates. In fact, a coarse moving bed of the solid sorbent can act as a filter to trap fly ash, and then release it as a concentrated stream of particulates. Further, heat exchange and temperature control within the bed is more easily handled with a moving bed, especially with a fluidized bed. Also, because the solid sorbent moves between the adsorption and regeneration vessels, numerous large valves, and the means of switching them every few hours, can be omitted from the process, with consequent savings in capital and maintenance costs. Another advantage is that a constant flow of regeneration offgas is obtained, rather than the intermittent flows associated with a swinging fixed bed operation. This can make the disposal of this offgas, e.g. in a Claus sulfur plant, much easier. Finally, changeout of sorbent is faster and more straightforward in a moving bed.

The ability of the preferred sulfur oxide sorbents to oxidize carbon monoxide allows a reduction in the amount of excess air used in the main combustor, since essentially complete CO combustion can be obtained in the downstream sorbent bed. Additional air can be added to the sorbent bed, as needed. The concentration of oxygen in the gas leaving the sorbent bed must be greater than 0.1 vol %, and preferably from about 1.0 to about 4.0 vol %. As noted above the amount of air fed to the combustor may fall below the stoichiometric amount needed to oxidize hydrocarbon fuel completely to water and carbon dioxide. In this case, the flue gas will contain large quantities (greater than 1.0 vol %) of carbon monoxide which will be oxidized in the sorbent bed. A fluidized bed with heat exchange (typically with coils for steam generation) is preferred for this application.

This reduction in excess air has at least two advantages. First, it will lead to cost reduction or increase in feed capacity of the combustor. The air blower and other components can be sized smaller, for the same fuel feed rate.

Second, running with less excess air or lower combustion temperature can result in lower NOx emissions from the combustor. Normally, it is difficult to take full advantage of this effect, because at these conditions, the production of carbon monoxide becomes large. This tradeoff between CO and NOx emissions is illustrated in FIG. 5, which shows NO effluent concentrations as a function of CO concentration, calculated using a model for a circulating fluid bed coal combustor. This graph is from "Modeling of NOx Formation in Fluidized Bed Combustion" presented by J. E. Johnson at the 16th IEA-AFBC meeting in Palo Alto, May 2, 1988. The graph indicates that the amount of combustion of air is selected to preferably maintain the concentration of carbon monoxide in the combustor effluent at greater than 500 ppm, and more preferably between about 600 ppm and about 5,000 ppm to minimize the amount of nitrogen oxide in this effluent stream.

Besides oxidizing CO, the oxidation promoters associated with the SOx sorbent should oxidize trace amounts of hazardous organic compounds, such as dioxins, in flue gas to more benign forms.

Although this description of the invention is with respect to flue gas from combustors such as used in coal-burning electric power plants, the solid sorbent described here could also be used for cleanup of effluent gas from a variety of processes, including hazardous waste incinerators and mineral and metallurgical operations.

The flue gas that results from the combustion or oxidation of sulfur-containing materials, including the fossil fuels used in generation of steam and electric power, typically contains SO_2 and SO_3("SOx"). SOx emissions are being regulated more strictly, since they are believed to contribute to acid rain and other environmental problems. Complete combustion is rarely achieved, so the flue gas from combustion of carbonaceous fuels typically contains some CO. The materials described here can remove both SOx (by adsorption) and CO (by oxidation to CO_2). Fitting a furnace or combustor with the process and the system of the present invention cheaper high-sulfur coal or oil for fuel may be used.

With reference to FIG. 1, there is shown a preferred fixed-bed system wherein a combustion flue gas from a coal combustor **11** using fuel **8** (e.g. coal) and an oxygen-containing gas (e.g. air) **9** to generate a desired energy. In this case, the output is steam **7**. Dependent on the type of fuel, e.g. hydrocarbon, coal, etc, the flue gas may contain in the order of 1,000 ppm of sulfur dioxide, 1,000 ppm of carbon monoxide, 15% carbon dioxide, 15% water, and the balance of nitrogen (with argon from the combustion air) and air. The flue gas stream **10** may have fed thereto a tailgas stream from an elemental sulfur recovery unit **70** (e.g. a Claus plant), and air **71** prior to being fed to stream **19** The temperature in the coal combustor is in the order of about 2,000° F.

A sulfur oxide enriched gas stream from the combustor **11** is fed by a line **19** through a valve **20**, a line **21** to a first solid adsorbent bed **22**. The outlet **23** of the first adsorbent bed **20** is connected through a valve **31**, a line **24**, to the inlet of a second solid adsorbent bed **25**. The output **26** of the second bed **25** is connected through a valve **27**, lines **28**, **29** to a stack **30**. The line **29** has a heat exchanger for removing heat from the line and using it to generate steam. Thus, the first **22** and second **25** beds are connected in series between the furnace **12** and the stack **30**, and adsorb therein the sulfur oxides from the sulfur oxide enriched stream **19**. The sulfur oxides are adsorbed in the form of inorganic sulfates or sulfur oxides or combinations thereof, and the sulfur oxide and carbon monoxide depleted stream is passed to the stack **30** by line **26**, valve **27** and line **28**.

The third solid adsorbent bed **32** is initially in a regeneration mode while the first and second beds are in an adsorbent mode. During regeneration, a stream of reducing gas from a source **33** travels by a line **34**, a valve **35** and a line **36** to the third bed to reduce the retained inorganic sulfates or sulfur oxides or combinations thereof to hydrogen sulfide and/or sulfur dioxide and thus form a hydrogen sulfide and/or sulfur dioxide bearing stream which is sent to a Claus plant (**70**) by a line **37**, a valve **38**, and a line **57**. Since regeneration of the third bed **32** will be completed before the first and second beds have adsorbed a desired amount of sulfur oxides, the third bed is preferably placed on standby by closing valves **35** and **38**.

When a predetermined adsorption distribution in the first and second beds requires that the first bed be removed from the series, the feeds to each of the beds are realigned such that the second bed **25** and the third bed **32** are placed in series between line **19** and the stack by first closing valves **20** and **31**, and opening valve **40** to disconnect the first bed **22** from the second bed **25** and to connect the sulfur oxide enriched stream from line **19** to the inlet of the second bed **25**. At the same time valve **41** is opened to serially connect the third bed to the second bed and valve **42** is opened to provide a path from the outlet line **37** of the third bed to the line **29** to the stack **30**.

As the second and third beds **25**, **32** are being connected in series, the first bed **32** is placed in a regeneration mode by opening valves **43**, **44** to provide a path for the reducing gas from the source **33**, the valve **43**, the line **22**, the first bed **22**, the line **23**, the valve **44** and the line **57** to the Claus plant **70**. The reducing gas then regenerates the first bed **22**, and forms a hydrogen sulfide and/or sulfur dioxide stream which is sent to the Claus plant **70** via line **39**. When the first bed is regenerated, the first bed is placed on standby by closing valves **43** and **44**.

When the second and third beds **25**, **32** have a predetermined adsorption distribution requiring that the second bed be removed from the series, the feeds to each of the beds are realigned such that the third and first beds **32**, **22** are connected in series. The valves **50**, **51**, **52** to provide a path for the sulfur oxide enriched gas stream **19** through valve **50**, line **36**, the third bed **32**, valve **51**, line **53** , to the inlet of the first bed **22**, and the valve **52**, the line **29**, to the stack **30**.

At the same time, the second bed is placed in a regeneration mode by opening valves **55**, **56** to pass reducing gas to the second bed **25**, and return the desorbed hydrogen sulfide and/or sulfur dioxide bearing stream to the Claus unit **70**. Thus, each one of the three beds are sequentially placed in an initial bed mode in the series, taken out of the series for a regeneration mode and then placed in a second bed mode in the series.

While in an adsorbent mode, each of the beds **22**, **25**, **32** operate at a temperature from about 900° F. to about 1,400° F. A temperature of from about 1,100° F. to about 1,300° F. is preferred. The oxygen content of the stream **19** entering the beds in an adsorbent mode is in an amount of from about 0.10 to about 10 vol %, preferably from about 2 to about 4 vol %. Pressure within each bed should be maintained at a pressure of from about 0.1 to about 10 atmospheres, preferably from about 1.5 to about 3.0 atmospheres. GHSV should be from about 500 to about 20,000, and preferably from about 3,000 to about 5,000 GHSV. An additional benefit of operating each bed during the adsorbent mode within these parameters is that any carbon monoxide therein is converted into carbon dioxide which is released into the environment.

The adsorbent in each bed can be in the form of balls, pebbles, spheres, extrudates, channeled monoliths, microspheres or pellets. This sulfur oxide-capturing adsorbent provides absorbers or acceptors which absorb, and collect, or otherwise remove sulfur oxides from the effluent gaseous stream. In one embodiment, the bed contains Mg/Al spinels.

The outlet conduits **23**, **26**, **37** are monitored by a sensor. A suitable sensor is a Siemens Ultramat **22P** infrared analyzer. Of course, as will be understood by those skilled in the art, other comparable analyzing equipment can be used.

Sulfur dioxide break-through occurs when a substantial increase in the concentration of sulfur dioxide occurs in one of the lines **23**, **26**, **37**. This increase may be in the order of from about 3 ppm to about 250 ppm in less than about 2 minutes.

During regeneration of each adsorbent bed **22**, **25**, **32** the temperature is maintained between about 900° F. to about 1,400° F.; and the pressure in the bed is maintained at about 0.10 to about 10 atmospheres, preferably about 0.5 to about 3 atmospheres. The reducing gas stream **33** is directed into the bed under regeneration is at a gas hourly space velocity (GHSV) of about 10 to about 1,000, preferably about 100 to about 150. Initially, a GHSV of about 300 is preferred when commencing regeneration of a fixed-bed adsorbent so that a higher concentration of liberated gases can be removed from the regenerator. As regeneration proceeds, the GHSV can be reduced to about 50 as the concentration of liberated gases diminishes. Similarly, although hydrogen is the preferred reducing gas for regeneration, other hydrocarbon reducing gases can be used. These will preferably comprise C_1 through C_5 hydrocarbons. Substantially improved regeneration results are anticipated when water **60** is co-fed into the bed along with the hydrocarbons. The hydrogen and/or

hydrocarbon stream **32** may contain 0.0 to 50% water. Syngas, a mixture of CO and hydrogen may also be used as a reducing gas.

COMPUTER SIMULATIONS

A computer simulation of adsorption fronts moving through fixed beds was written to explore the benefits of various process configurations. The computer model uses a shrinking core model, cast in cylindrical geometry, to described the SOx uptake by an individual particle. This model is described in reference works such as "Chemical Reactor Analysis and Design" by G. F. Froment and K. B. Bischoff (John Wiley and Sons, New York, 1979). The parameter values for the simulations were found to fit the breakthrough results in a laboratory reactor, with some allowance for sorbent aging. The operating conditions (e.g. bed length, flow rates, feed concentration) are suitable for a full scale embodiment.

For these experiments, the operating pressure and temperature were 1.1 atmospheres and 1,200° F. Other assumptions were a feed concentration of SO_2 of 0.43 vol %, gas velocity of 105 cm/sec, and an uptake capacity of the sorbent at long times of 46.5 SOx (as SO_3) per gram of fresh sorbent. The bed density was 0.707 g/cm^3. The dimensionless parameter of effective diffusivity divided by the particle radius, and by the mass transfer coefficient had a value of 0.11. The maximum SO_2 concentration permitted in the effluent from the system was 1 ppm.

In the base case, the sorbent was distributed in two beds each having a 135 cm length. While one bed was on adsorption duty, the other was being regenerated or was on standby after regeneration. It takes a shorter period of time to regenerate then to complete an adsorption cycle. In the second case which is an embodiment of the present invention, the same amount of sorbent was distributed in three beds, each 90 cm long.

TWO-BED SYSTEM

From the time the feed was introduced to the first 135 cm bed until the time the effluent SO_2 concentration reached 1 ppm, was 1,118 min (18.6 hr). At this point adsorption on this bed was stopped, and the bed was switched to regeneration; while the other (regenerated) bed was switched into adsorption service. The total SOx loading on the first bed at this point was 36.8 wt. %, therefore only 79.1% of the total uptake capacity of the sorbent could be utilized in this system. Each bed would be cycled once every 37.2 hr (i.e., 2×18.6 hr). This higher cycling rate results from less than 100% sorbent capacity utilization which can lead to faster sorbent deactivation.

Another disadvantage of the two-bed system of operation is that the beds are not switched until the SO_2 effluent concentration actually approaches the allowable limit. This makes for vulnerability to excessive emissions if a process upset should occur near the switching time. A partial solution to this problem would be to switch beds well before the effluent SO_2 concentration approaches the emission limit. However, this would have the effect of reducing sorbent capacity utilization even further.

Still another disadvantage of the two-stage system is that if significant SO_2 breakthrough at the bed exit is not permitted to occur, it can be difficult to monitor the condition of the sorbent, or even know how close the sorption front is to breakthrough. Thus, the operator would not know how much spare capacity is available in the bed.

THREE-BED SYSTEM

The three-bed system of the present invention solves the above-noted problems with the conventional 2-bed system. For comparison in model calculations, the same amount of sorbent was used as in the two-bed system, but was distributed in 3 beds, each 90 cm long. Two out of the three beds were always in series performing adsorption, while a third bed was on regeneration or standby following regeneration. At the time of valve switching, the first bed in the adsorption train switches to a regeneration mode, the second bed is moved to the first bed position, and the recently regenerated bed becomes the second bed in the adsorption train.

Operation of the three-bed system significantly differs from the two-bed system. As long as the length of the adsorption front within the beds is less than the length of a single reactor, nearly 100% sorbent utilization can always be attained. For this case, which is typical, the preferred time to switch reactors is when the SO_2 concentration in the effluent from the first bed reaches 95–100% of the feed concentration. At this point, the first bed is essentially saturated and is no longer sorbing much SOx. The adsorption front is then contained within the front section of the second bed. In other words, the preferred valve switching point is when the adsorption front has nearly completed passage past the exit of the first bed in the series. This contrasts with the 2-bed system where the usual valve switching point is just before the adsorption front starts passage out the exit of the single bed on adsorption duty.

The velocity of the adsorption front as it moves through a bed can be calculated from a simple mass balance:

$$\text{Front. vel.} = \frac{\text{(gas velocity)}(\text{SO2 molar feed conc.})(80\ \text{g/mol SO3})}{\text{(sorbent bulk density)(sorbent uptake capacity)}}$$

For the conditions used in this simulation, the front velocity was 0.0955 cm/min. For a 90 cm bed length, the preferred bed switching time (i.e. the time for the front to propagate one bed length) was 15.7 hr. Therefore, each bed would be regenerated every 47.1 hr (=3×15.7 hr).

One advantage of the three-bed system is that the sorbent capacity is fully utilized. This translates into less frequent cycling of the sorbent, which can extend sorbent lifetime. Also, more deterioration in sorbent performance can be tolerated, since the intrinsic sorbent capacity is better utilized.

Another advantage of the three-bed system is that the full adsorption front can be allowed to break through the first bed. Monitoring of the timing and shape of this breakthrough curve can furnish valuable information on the state of the sorbent and on other developments such as nonideal flow patterns in the bed.

A third advantage of the three-bed system is that, at the time of bed switching, the adsorption front is contained in the front section of the second bed. The adsorption front, defined as the distance along the bed from a point where the SO_2 concentration in the gas phase drops below 99% of the feed concentration to where the SO_2 concentration drops to 1 ppm. For the example herein, the absorption front is about 43 cm long. Thus, at the preferred switching time, this front extended from the front of the second bed to a point 43 cm from its entrance. This left 47 cm (more than half the bed) as spare capacity in case of a process upset. For instance, if the switching event had to be delayed, adsorption could have continued anther 8.2 hours before 1 ppm SO_2 started to emerge in the effluent of the second bed.

It should be noted, however, that if subsequent cycles reverted immediately to the normal 15.7 hr switching interval, the adsorption front at the time of valve switching would remain at the exit of the second bed, leaving no spare capacity for further upsets. In order to move the location of the adsorption front (at the time of valve switching) to its preferred location near the entrance of the second bed, the next several valve switching must be made at intervals of less than 15.7 hr.

The three-bed system embodiment of the present invention provides a significant improvement in the configuration of the fixed-bed process, and economically reduces combustion flue gases and Claus tailgas effluent concentrations of sulfur and CO below the levels attained with current treatment technologies.

FIG. **2** is an example of a steep front case. The initial bed in the series is saturated to the exit of the bed. In this case the adsorption front is steep enough that it does not extend more than half-way into the second bed. This case provides almost total utilization of the initial bed, and then the initial bed is switched out of the adsorption mode and into a regeneration mode.

In a shallow adsorption front case shown in FIG. **3**, which might arise with high gas flow rates and/or large particles, it is possible that the leading edge of the second bed is not yet saturated, e.g. the first bed may only be at an 80% adsorption level. However, in the second case, there still is an advantage by splitting into two beds.

If gas flows slower and/or particles are smaller then the more steep the front. Conversely, the faster the gas and/or the larger the particle, the more shallow the slope of the adsorption rate front.

STRATEGIES FOR SWITCHING BEDS

In the case of a very steep adsorption front, the system would switch the first bed from an adsorption mode to a regeneration mode when the effluent from the first bed reached about 95% of inlet concentration, because the first bed is almost totally saturated and there is little frontal penetration into the second bed. This defines one case of a predetermined adsorption distribution.

In the case of a very shallow adsorption front, there may be break through at the end of the second even though the first bed is not yet saturated. Thus, there is a need to monitor the exit from the second bed. The very shallow front defines a second case of a predetermined adsorption distribution.

In the intermediate case, which may be the most common, the effluent from the first bed is monitored and a mathematical model, such as the one used to calculate the results of this application, is used to predict or extrapolate what the shape of the adsorption front is in the second bed. To provide a margin of safety and to define a third case of a predetermined adsoprtion distribution, switching preferable occurs before the adsorption front reaches the end of the second bed, for example at 80% into the second bed.

Leading edge of the sloped adsorption front show adsorption levels at specific locations in the beds. The relatively flat trailing portion of the curve indicates that the bed(s) is saturated.

FLUIDIZED BED SYSTEM

With reference to FIG. **4**, there is shown a fluidized bed system comprising a reactor **136**, a regenerator **137**, a conduit **138** for feeding spent adsorbent from the reactor **136** to the regenerator **137**, and another conduit **139** for passing a fluidized bed of regenerated adsorbent from the regenerator **137** to the reactor **136**. A sulfur oxide enriched stream **140** from the coal combustor **11** in FIG. **1** is fed to the lower end of the reactor **136**, over adsorbent therein to strip out the sulfur oxides and provide a sulfur oxide and carbon monoxide depleted stream **141** for an incinerator or a stack. A hydrogen bearing or other reducing gas stream **142** is fed to the bottom of the regenerator **137** to reduce the sulfur compounds on the spent adsorbent to hydrogen sulfide and form a hydrogen sulfide and/or sulfur dioxide bearing outlet stream **143**.

Operating parameters for the fluidized system are substantially the same as those described above with respect to the FIGS. **1** fixed-bed embodiment. Further, the operating conditions for the furnace **12** are similar when using either the fluidized or fixed bed systems. The temperature in the fluidized bed reactor **136** is maintained at from about 900° F. to about 1,400° F. preferably between about 1,100° F. to about 1,300° F. The oxygen content of the stream **140** introduced into the reactor **140** is maintained in an amount of from about 0.1 to about 10 vol %, preferably 2 to about 4 vol %. Pressure in the reactor **136** should be maintained at about 0.1 to about 10 atmospheres, preferably about 1.5 to about 3 atmospheres. The GHSV should be maintained at about 400 to about 7,000, preferably about 500 to about 2,500.

FCC REGENERATOR IN PARTIAL CO COMBUSTION MODE

Known SOx adsorbing additives which circulate with the catalyst between the reactor **200** and regenerator **202** in the FCC unit perform best when there is an adequate supply of excess oxygen in the regenerator **202**. This oxygen is probably needed to convert SO_2 to SO_3, which is more readily sorbed by the circulating additive. However, this oxygen requirement may force a refiner to supply more oxygen than otherwise desired to the FCC regenerator **202**.

There are substantial benefits to running the regenerator **202** in a partial CO combustion mode, that is, with insufficient oxygen to convert all CO to CO_2. As noted above, the uncombusted CO is typically burned in a high-temperature CO boiler. In a partial CO combustion mode, the catalyst is not heated as much in the regenerator **202**, which can help keep the regenerator temperatures down in a heat-balanced FCC unit. This may be particularly helpful when the FCC unit is processing heavy feeds, which tend to make a lot of coke on the FCC catalyst. However, the option of running with partial CO combustion can be greatly restricted if the FCC unit depends on a circulating additive for SOx abatement, because, as noted above, the SOx sorbents tend to be more effective in the presence of excess oxygen.

Therefore, it is more practical to optimize FCC reaction conditions if the requirements of a circulating additive for adsorbing SOx do not need to be considered. Also, a circulating SOx absorbing additive tends to dilute the active cracking catalyst. In addition, the optimum operating conditions for sulfur gas adsorption and desorption can be more readily met by a separate, dedicated sorption system. Replacing the typical CO boiler with a separate unit for desulfurization as shown in FIGS. **6** and **7** is thus especially useful when it is desired to run the FCC regenerator in a partial CO combustion mode, but effective SOx abatement is needed.

With reference to FIG. **6**, there is shown an FCC unit comprising a reactor **200** and a regenerator **202**. Fresh preheated gas oil feed **203** is typically fed to the bottom of the reactor **200**. A bed of fluidized catalyst flows upwardly in the reactor with the feed and provides cracked product **204** as an overhead. The fluidized catalyst is fed by a line **205** to the regenerator **202**. The regenerator is also fed with combustion air by a conduit **206** which burns coke from the catalyst in the regenerator **202**. Regenerated catalyst is returned to the reactor **200** by a conduit **207**. When the regenerator **202** is run in a partial combustion mode, the fluegas stream in an overhead line **208** is typically fed to a CO boiler (not shown) where combustion air oxidizes CO to CO_2 and the heat produced is used to generate steam.

The regenerator fluegas stream **208** includes SOx and CO because any hydrogen sulfide fed to the regenerator **202** with the catalyst by the conduit **205** is completely converted to SOx in the regenerator. The sulfur oxide and CO containing gas stream **208** from the regenerator **202** is optionally cooled in a heat exchanger **213** to within a range of from about 900° F. to about 1400° F. and is fed by a line **219** to a first fixed-bed reactor **220** containing a solid absorbent bed **222**.

The solid absorbent bed **222** absorbs substantially all of the sulfur oxide from the sulfur oxide enriched gas stream **18** and converts the CO to CO_2 to provide a SOx and CO depleted gas stream through outlet conduit **24**. The SOx and CO depleted stream is fed through a valve system (not shown) to a line **225** leading to an incinerator or to a stack.

While in an absorbent mode, the reactor **220** is operated at a temperature from about 900° F. to about 1,400° F. A temperature of from about 1,100° F. to about 1,300° F. is preferred. The oxygen content of the stream **219** entering the absorbent bed **222** is in an amount of from about 0.10 to about 10 vol %, 2 to about 4 vol % is preferred. Pressure within the reactor **200** should be maintained at a pressure of from about 0.1 to about 10 atmospheres, preferably from about 1.5 to about 3.0 atmospheres. GHSV should be from about 500 to about 20,000, and preferably from about 3,000 to about 5,000 GHSV. Operating the reactor **220** during the absorbent mode within these parameters converts substantially all carbon monoxide therein into carbon dioxide which is released into the environment. Other gases released from the reactor **220** include nitrogen, oxygen, and trace amounts of sulfur dioxide along with water.

The absorbent can be in the form of balls, pebbles, spheres, extrudates, channeled monoliths, microspheres or pellets. This sulfur oxide-capturing absorbent provides absorbers or acceptors which absorb, and collect, or otherwise remove sulfur oxides from the influent gaseous stream. In one embodiment, the bed **222** is Mg/Al spinels.

The outlet conduit **224** is monitored by a sensor **226** until sulfur dioxide break-through occurs. A suitable sensor is a Siemens Ultramat 22P infrared analyzer. Of course, as will be understood by those skilled in the art, other comparable analyzing equipment can be used.

Sulfur dioxide break-through occurs when a substantial increase in the concentration of sulfur dioxide occurs in the conduit **224**. This increase will be in the order of from about 3 ppm to about 250 ppm in less than about 2 minutes.

When sulfur dioxide break-through is detected, the SOx and CO containing gas stream **219** is directed through a suitable valve system (not shown) into a second fixed-bed reactor **228** having a solid absorbent bed **230** therein. Concurrently, the valve system directs a hydrogen rich stream **232** to the first reactor **220** for regenerating the first absorbent bed **222**. The hydrogen rich stream **232** may contain hydrogen and/or hydrocarbons and/or syngas.

During regeneration of the absorbent bed **222** the temperature is maintained between about 900° F. to about

1,400° F.; and the pressure in the reactor **220** is maintained at about 0.10 to about 10 atmospheres, preferably about 0.5 to about 3 atmospheres. The H_2 and/or hydrocarbon and or syngas stream **232** is directed into the reactor **220** at a gas hourly space velocity (GHSV) of about 10 to about 1,000, preferably about 100 to about 150. Initially, a GHSV of about 300 is preferred when commencing regeneration of a fixed-bed absorbent so that a higher concentration of liberated gases can be removed from the regenerator. As regeneration proceeds, the GHSV can be reduced to about 50 as the concentration of liberated gases diminishes.

Similarly, although hydrogen is the preferred reducing gas for regeneration, other hydrocarbon reducing gases can be used. These will preferably comprise C_1 through C_5 hydrocarbons. Substantially improved regeneration results are anticipated when water is co-fed into the reactor along with the hydrocarbons. The hydrogen and/or hydrocarbon and/or syngas stream **232** may contain 0.0 to 50% water. Also, syngas typically contains at least 10% hydrogen and at least 10% CO.

Regeneration of the bed **222** provides a hydrogen sulfide and/or sulfur dioxide bearing stream through the outlet conduit **224**, the valve system (not shown), and via line **234** to the sulfur plant for recovery of sulfur. The hydrogen sulfide and/or sulfur dioxide bearing stream may also contain water and unconverted reducing gas.

The sulfur oxide and CO containing stream **219** and the hydrogen and/or hydrocarbon and/or syngas bearing stream **232** are alternately fed to each one of the reactors **220, 228**, whereby each bed **222, 230** is first spent by sulfur oxides extracted from the stream **219**, and then regenerated by the hydrogen and/or hydrocarbon and/or syngas bearing stream **232**.

With reference to FIG. **7**, there is shown an FCC unit comprising a reactor **200** and regenerator **202** wherein elements having the same reference numerals as in FIG. **6** operate in the same manner as described above with reference to FIG. **6**. The regenerator fluegas stream **208** is fed to a fluidized bed system comprising a reactor **240**, a regenerator **242**, a conduit **244** for feeding a fluidized bed of spent absorbent from the reactor to the regenerator **242**, and another conduit **246** for passing a fluidized bed of regenerated absorbent from the regenerator **242** to the reactor **240**. The sulfur oxide and CO containing stream **208** from the FCC regenerator **206** is fed to the lower end of the reactor **240**, and mixed with the fluidized bed of absorbent therein to strip out the sulfur oxides and convert the CO to CO_2, and to provide a SOx and CO depleted stream **250** for the incinerator or the stack. A hydrogen bearing stream **252** is fed to the bottom of the regenerator **242** to reduce the sulfur compounds on the spent absorbent to hydrogen sulfide and form a hydrogen sulfide and/or sulfur dioxide bearing outlet stream **254** which can be suitably sent to a sulfur recovery plant such as a Claus unit.

Also, since conversion of CO to CO_2 produces a high temperature, an air stream **260** and a fuel gas stream **261** are provided to further increase the temperature and water **262** fed to a line **264** is converted to steam as an output **263**.

Operating parameters for the fluidized adsorbing system are substantially the same as those described above with respect to the FIG. **6** fixed-bed embodiment. The temperature in the fluidized bed reactor **240** is maintained at from about 900° F. to about 1,400° F., preferably between about 1,100° F. to about 1,300° F. The oxygen content of the stream **208** introduced into the reactor **240** is maintained in an amount of from about 0.1 to about 10 vol %, preferably 2 to about 4 vol %. Pressure in the reactor **240** should be maintained at about 0.1 to about 10 atmospheres, preferably about 1.5 to about 3 atmospheres. The GHSV should be maintained at about 400 to about 7,000, preferably about 500 to about 2,500.

If the regenerator **202** is operated in full combustion or on the brink of full combustion where the main emphasis is on converting sulfur species to SOx, and a minor requirement to convert CO, then the SOx adsorber may be either a fixed bed or a moving or fluid bed. When less than one (1) vol % of CO is produced in the regenerator **202**, the fixed bed embodiment is preferably used.

When operating the regenerator **202** in deep partial combustion with a large amount of combustibles (CO) and oxygen coming together in a fixed bed (**220, 228**), there may be a risk of exotherms. Consequently, the moving or fluidized bed **240** is preferred when operating the regenerator **202** in deep partial combustion because the heat can be readily removed from the bed and distributed for other refinery uses.

As noted above, replacing a typical CO boiler with a separate unit for desulfurization as shown in FIGS. **6** and **7** is especially useful when it is desired to run the FCC regenerator in a partial CO combustion mode, but effective SOx abatement is needed. For such a case, air **260**, in an amount to combust all the CO to CO_2 is needed. Additionally, it is preferred to have a sufficient quantity to result in 0.1–10% excess O_2 by volume, is fed to the reactor **240** along with the FCC fluegas **208**. A considerable quantity of heat is released upon combustion of the CO in the FCC fluegas in the reactor **240**, so provision is preferably made for heat removal from the solids bed reactor **240**. This is most easily accomplished if the bed consists of moving solids as provided in FIG. **7**, either granular (particle size about 1–10 mm) or fluidized (particle size about 0.02–0.5 mm). Heat exchanger tubes **264**, typically for raising steam by a water feed **262** and steam outlet **263**, can be installed in such beds, and rates of heat transfer are high. The temperature in the reactor **240** can be further increased by adding a fuel gas stream **261** thereto. Heat can also be removed from the fixed bed of FIG. **6** by a similar heat exchange.

As demonstrated by the following Example 6 SOx sorbents in accordance with the present invention can oxidize CO to CO_2. Platinum is a preferred promoter for this reaction. Platinum is also beneficial in the SOx sorption, probably because it promotes the oxidation of SO_2 to SO_3.

Moving granular beds have several advantages over to finer, fluidized beds. The pressure drop tends to be lower through a moving granular bed, and moving granular beds are known to trap fine particulates, such as the catalyst fines in the regenerator fluegas **208**. Thus, a granular bed might function to decrease the release of SOx, CO and particulates. The fine particulates (i.e. FCC catalyst fines) could be disengaged from the granular solids in a riser-type regenerator **242**, and finally collected using a relatively small cyclone separator located in the line **246** between the regenerator **242** and the adsorbent reactor **240**.

However, the technology for handling fluidized solids is already in place at an FCC complex, so that it may be more convenient to handle fluidized solids rather than granular solids. Also, solids for adsorbing SOx are more readily made available in spray-dried fluidized form. Also, catalyst coolers for heat exchange are commercially available for fluidized solids.

If the offgas in the lines **234** or **254** from the reductive regeneration of a SOx sorbent is sent to an amine scrubber

270, along with FCC fuel gas **252**, the preferred form in which to desorb sulfur would be as H_2S. SO_2 may have deleterious effects on the amine scrubber, and if both H_2S and SO_2 are formed simultaneously, they can react via the Claus reaction to form elemental sulfur, which can foul the transfer lines downstream.

On the other hand, if the offgas in lines **234** or **254** is fed directly to a Claus unit **270**, the preferred form of sulfur is as SO_2, since SO_2 formation minimizes the amount of reducing gas consumed during sorbent regeneration and feeding SO_2 to the Claus unit decreases the amount of air required by the Claus plant to process its H_2S feed. Another potential advantage of producing SO_2 is that it could be absorbed in a water spray tower **271**, which can be cheaper than the amine system needed for H_2S absorption. The SO_2 could subsequently be recovered from the water in a concentrate form and without substantial hydrocarbon impurities by heating the SO_2/water solution in a unit **272**.

Therefore, if mainly making H_2S it is preferable to use an amine unit. If mainly making SO_2 then it is preferable to use water adsorption. In each case, the sulfur species can be adsorbed in a liquid and then pumped through refinery conduits, or otherwise transported to a desired unit such as a sulfur plant at a remote location. But if the unit is close to a sulfur plant, the stream may be pumped directly into the plant. At the sulfur plant all of the streams can be fed to plant, or preferably, the sulfur species can be stripped out and then fed into plant as a gas.

Accordingly, the invention contemplates embodiment wherein sulfur gases coming off desorption are adsorbed in a liquid (e.g. water) for transport to a sulfur plant. At the plant all of the streams can be fed to plant, or preferably, the sulfur species can be stripped out and then fed into plant as a gas.

Therefore, control of the offgas composition is advantageous. This control can be obtained by proper choice of sorbent, adsorption conditions, and desorption conditions. In general, higher adsorption temperatures, higher sulfur loadings on the sorbent, and use of hydrogen as the reductant all favor SO_2 production.

ADSORBENTS

Non-limiting examples of suitable solid adsorbents for use in the embodiments of the present invention include the porous solids, alumina, silica, silica-alumina, natural and synthetic zeolites, activated carbon, spinels, clays, and combinations thereof. Gamma alumina, chi-eta-rho alumina, delta alumina, and theta alumina are particularly useful as adsorbents and supports because of their high surface areas.

While alpha alumina and beta alumina can be used as adsorbents, they are not as effective as gamma, chi-eta-rho, delta and theta alumina. One or more oxides of other metals can also be used as adsorbents, either alone or in combination with alumina or as spinels, such as bismuth, manganese, yttrium, antimony, tin, copper, Group IA metals, Group IIA metals, rare earth metals, and combinations thereof. Magnesium aluminate spinels are particularly useful as adsorbents. These may be magnesium or aluminum rich with magnesium aluminate spinels preferred. Lanthanum and cerium are preferred rare earth metals. Naturally occurring rare earths, such as in the form of baestenite, are also useful adsorbents. Elemental copper or copper compound adsorbents, such as copper oxide adsorbents, can also be used. The copper oxide can be cuprous oxide and/or cupric oxide. Other copper compounds can be used, such as copper (II)

sulfate, copper (II) acetate, copper (II) formate, copper (II) nitrate and/or copper (II) chloride. The adsorbents can also be a blend/mixture of high density and low density materials.

Also, a metal or metal oxide may be deposited on the solid adsorbent or may be used alone. The metal or metal oxide part of the adsorbents can be supported, carried and held on a refractory support or carrier material which also provides part of the adsorbents. The support controls the attrition and surface area characteristics of the adsorbents. The support preferably has a surface area greater than about 10 m^2/g and most preferably from about 50 m^2/g to about 500 m^2/g for best results. Suitable supporters include, but are not limited to, silica, alumina, kaolin or other clays, diatomaceous earth, boria, and/or mullite. The support can comprise the same material as the metal or metal oxide part of the adsorbents.

The adsorbents can be impregnated or otherwise coated with at least one oxidizing catalyst or promoter that promotes the removal of nitrogen oxides, the oxidation of SO_2 to SO_3 in the presence of oxygen, and the regeneration of the sorbent. It is believed that SO_3 is more readily adsorbed than SO_2. One useful catalyst is ceria (cerium oxide). Another useful catalyst is platinum. Other catalytic metals, both free and in combined form, preferably as an oxide form, can be used, either alone or in combination with each other or in combination with ceria and/or alumina, such as rare earth metals, metals from Group 8 of the Periodic Table, chromium, vanadium, rhenium, tungsten, silver and combinations thereof. The promoter can comprise the same material as the adsorbent. An even distribution of the promoter is preferred for best results and to minimize adsorbent erosion.

Useful Group IA metals include lithium, sodium, potassium, rubidium, and cesium. Useful Group IIA metals include magnesium, calcium, strontium, and barium. Useful Group VIII metals are the Group VIII noble metals (the platinum family of metals) including ruthenium, rhodium, palladium, osmium, iridium, and platinum. The rare earth metals are also useful and are referred to as the lanthanides. Suitable rare earth metals include cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium.

Preferably, the promoter may be selected from the rare earth metals, the platinum group metals and mixtures thereof. Particularly good results are achieved when the promoter is cerium and/or platinum, with cerium giving outstanding results.

A second promoter, if present, may be selected from the metal or the metal oxide form of iron, nickel, titanium, chromium, manganese, cobalt, germanium, tin, bismuth, molybdenum, antimony, vanadium and mixtures thereof. More preferably, the second promoter is selected from iron, nickel, cobalt, manganese, tin, vanadium and mixtures thereof. Additional metals may be also incorporated into the sorbent. For example, the sorbent may include small or trace amounts of additional metals or metal oxides, such as lanthanum, iron, sodium, calcium, copper, and titanium.

The specific amounts of the promoters included in the solid sorbent, if present at all, may vary widely. Preferably, the first promoter is present in an amount between about 0,001% to about 20% by weight, calculated as elemental metal, of the solid sorbent, and the second promoter is present in an amount between about 0.001% to about 10% by weight, calculated as elemental metal, of the solid sorbent. Preferably, the solid sorbent includes about 0.1% to about 20%, more preferably about 0.2% to about 20%, and still more preferably about 0.5% to about 15%, by weight of rare earth metal, calculated as elemental metal. Of course, if a platinum group metal is employed in the solid sorbent, very much reduced concentrations (e.g., in the parts per thousand to parts per million (ppm) range) are employed. If vanadium is included as the second promoter, it is preferably present in an amount of about 0.01% to about 7%, more preferably about 0.1% to about 5%, and still more preferably about 0.5% to about 2% by weight of vanadium, calculated as elemental metal.

The promoters may be associated with the solid sorbent using any suitable technique or combination of techniques; for example, impregnation, coprecipitation, ion-exchange and the like, well known in the art. Also, the promoters may be added during synthesis of the sorbent. Thus, the promoters may be an integral part of the solid sorbent or may be in a phase separate from the solid sorbent (e.g., deposited on the solid sorbent) or both. These metal components may be associated with the solid sorbent together or in any sequence or by the same or different association techniques. Cost considerations favor the preferred procedure in which the metal components are associated together with the sorbent. Impregnation may be carried out by contacting the sorbent with a solution, preferably an aqueous solution, of the metal salts.

It may not be necessary to wash the sorbent after certain soluble metal salts (such as nitrate, sulfate or acetate) are added. After impregnation with the metal salts, the sorbent can be dried and calcined to decompose the salts, forming an oxide in the case of a nitrate, sulfate or acetate.

The above-mentioned adsorbents are discussed in U.S. Pat. No. 4,692,318, which patent is hereby incorporated herein by reference.

In one general aspect, the present invention may involve use of a sorbent which is represented by the following empirical formula: $Mg_xAl_yO_z$, where the atomic ratio of x to y ranges from about 0.1 to about 10, and where z is at least as required to accommodate the valances of the Mg and Al components of the sorbent. This sorbent may have the spinel structure, and may contain one or both promoters described above.

Metal-containing spinels according to the above empirical formula that are useful in the present invention include the alkaline earth metal spinels, in particular magnesium (first metal) and aluminum (second metal)-containing spinel. Other alkaline earth metal ions, such as calcium, strontium, barium and mixtures thereof, may replace all or a part of the magnesium ions. Similarly, other metal ions, such as iron, chromium, vanadium, manganese, gallium, boron, cobalt, Group IB metals, Group IV metals, Group VA metals, the platinum group metals, the rare earth metals, Te, Nb, Ta, Sc, Zn, Y, Mo, W, Tl, Re, U, Th and mixtures thereof, may replace all or a part of the aluminum ions, preferably only a part of the aluminum ions.

The metal-containing spinels useful in the present invention may be derived from conventional and well known sources. For example, these spinels may be naturally occurring or may be synthesized using techniques well known in the art. Thus, a detailed description of such techniques is not included herein. A particularly useful process for preparing the solid sorbent is presented in U.S Pat. No. 4,728,635, the specification of which is incorporated by reference herein.

The Group IA, IIA, IB metals, Group IIB metals, Group IV metals, Group VA metals, Group VIA, and Group VIII metals referred to herein are those listed in the Periodic Table of the Elements in the *Handbook of Chemistry and Physics* (61st Edition).

Free magnesia and/or alumina (i.e., apart from the alkaline earth metal containing spinel) also may be included in the present solid sorbent, e.g., using conventional techniques. For example, in one embodiment, the solid sorbent preferably includes about 0.1% to about 30% by weight of free magnesia (calculated as MgO).

As mentioned above, potential solid adsorbents are magnesia rich, magnesium aluminate spinels. One example of such a spinel is a commercial magnesia rich, magnesium aluminate spinel containing 0 to 100 wt. % excess magnesia, 5 to 15 wt. % cerium, and 1 to 5 wt. % vanadium. These adsorbents are substantially described in U.S. Pat. Nos. 4,790,982; 4,472,267; and 4,469,589. The disclosures of U.S. Pat. Nos. 4,790,982; 4,472,267; and 4,469,589 are hereby incorporated herein by reference. Another particularly suitable adsorbent is a magnesium-aluminum spinel with excess magnesia (MgO), and with added RE and other metals, particularly with about 13 wt. % RE, about 0.5 wt. % La, about 13 wt. % CeO_2 and about 1.5 wt. % V in a 1/16" extrudate. In general, the magnesium aluminate spinels useful in the present invention may be prepared by methods which are conventional and well known in the art.

The following examples are illustrative of sorbents suitable for use in the reactor beds of the present invention.

EXAMPLE 1

A ceria/alumina sorbent was prepared by impregnating high pore value gamma alumina (1/8" extrudate from Dycat International) with a solution of 32.7 grams $Ce(NO_3)_6.6H_2O$ from Aldrich Chemical Company in 45 grams of water, using an incipient wetness technique. The material was dried for three hours at 120° C. (248° F.) and calcined one hour at 700° C. (1,292° F.), in air. The composition was approximately 11% CeO_2/Al_2O_3. This material was crushed and sieved to 14/60 mesh (API).

EXAMPLE 2

A magnesium aluminate sorbent was prepared, starting with two solutions. Solution I contained 461.5 grams magnesium nitrate, 68.6 grams of concentrated nitric acid, and 500 mls of water. Solution II contained 209.7 grams sodium aluminate, 10.7 grams sodium hydroxide, and 500 mls of water. To Solution I were added 2 liters of water, and then over a 30 minute period, Solution II. Sodium hydroxide was then added in an amount to bring the pH up to 10.7. The resulting mixture was aged for 16 hours and then filtered. The recovered solids were dried at 170° C. (338° F.) for 12 hours and sized to 14/60 mesh (API). This material had a composition of about $Mg_2Al_2O_5$.

EXAMPLE 3

To make a sorbent with approximately 100 ppm platinum loading, 35 grams of the magnesium aluminate from Example 2 was impregnated using an incipient wetness technique with a solution of 0.013 gram of chloroplatinic acid (37% Pt. assay) in 16 mls of water. The resulting solids were calcined in air at 450° C. (810° F.) for three hours and sized to 14/60 mesh (API).

EXAMPLE 4

A sorbent with approximately 10% ceria loading on magnesium aluminate was prepared by adding a solution of 9.71 grams cerium nitrate in 16 mls of water to 35 grams of magnesium aluminate from Example 1, using an incipient wetness method. The material was then dried for three hours at 120° C. (248° F.), calcined in air one hour at 700° C. (1,292° F.), and sized to 14/60 mesh (API).

To test the sorbents' ability to sorb sulfur oxides from a gas mixture simulating an incinerated Claus tail-gas, 6 grams of each material described in Examples 1–4 were loaded in an 11 mm I.D. quartz reactor with a central thermowell. The reactor was placed in a radiant furnace for rapid heating and cooling. A gas flow of 360 cc/minute with a composition of 1% sulfur dioxide, 4% oxygen, and 95% nitrogen (on a dry basis) was established through the reactor, after the desired sorption temperature was attained. Water, in the amount of about **20%** of the gas flow, as added by directing part of the feed gases through a saturator held at about 150° F.

The sulfur dioxide content in the effluent stream was monitored with a Siemens Ultramat **22P** infrared analyzer. A cold trap between the reactor and the analyzer removed most of the water on the effluent stream. Sorption experiments were terminated when the sulfur dioxide level in the effluent exceeded 250 ppm. Sulfur dioxide breakthrough was relatively sharp. In general, the analyzer detected no sulfur dioxide for the first 80–90% of the sorption period. Sulfur dioxide concentration of less than 2 ppm during this portion of the sorption was confirmed by measurements with Drager gas measurement tubes. The calculated weight percentage uptake of sulfur oxide as SO_3 during the sorption period is reported in the Table below.

Regeneration of the solid sorbent was accomplished by contacting it with hydrogen, which was bubbled through a saturator to obtain about 25% water vapor content. The composition of the off-gas during reductive regeneration was determined by injections on to a Hewlett-Packard 5890 gas chromatograph equipped with a thermal conductivity detector. Usually, both hydrogen sulfide and Sulfur dioxide could be detected in the off-gas, but typically one gas or the other dominated, depending on the sorbent and on operating conditions, as indicated in the following Table.

TABLE

Sorbent Material Identity	Temperature of Sorption and Regeneration, °F.	Wt % Uptake During Sorption	Dominate Sulfur Compound In Regeneration Off-Gas
CeO_2/Al_2O_3 (Ex. 1)	1,000	4.8	H_2S
CeO_2/Al_2O_3	1,200	6.2	SO_2
$Mg_2Al_2O_5$ (Ex. 2)	1,200	4.7	H_2S
$Pt/Mg_2Al_2O_5$ (Ex. 3)	1,200	33.8	SO_2
$CeO_2/Mg_2Al_2O_5$ (Ex. 4)	1,100	14.7	H_2S
$CeO_2/Mg_2Al_2O_5$	1,200	25.2	SO_2

The uptake of SO_x was greater for $Mg_2Al_2O_5$ promoted with Pt (Ex. 3) and with CeO_2 (Ex. 4) was higher than for $Mg_2Al_2O_5$ alone (Ex. 2). For the ceria-promoted materials of Examples 1 and 4, magnesium aluminate was a more effective sorbent than alumina, and increasing the operating temperatures from 1000° F. to 1200° F. (Ex. 1), and from 1100° F. to 1200° F. (Ex. 4) increased SO_x sorption which shifted the dominant off-gas sulfur species from H_2S to SO_2.

EXAMPLE 5

The carbon monoxide oxidation activity of two sorbents was tested by flowing a mixture of 4% carbon monoxide, 4% oxygen, and 8% carbon dioxide at a flow rate of 310 cc/min over 6 grams of each material in an 11 mm I.D. quartz reactor. Carbon monoxide and carbon dioxide concentration, as a function of reactor temperature, were monitored by Beckman Model 864 infrared analyzers. With the magnesium aluminate of Example 2, carbon monoxide was half converted at about 770° F. and substantially all converted at 860° F. With the platinum-promoted magnesium aluminate of Example 3, carbon monoxide was half converted at about 510° F. and substantially all converted at 540° F. With an empty reactor, there was no detectable carbon monoxide conversion for temperatures up to 1,200° F.

This example demonstrates that the designated sorbents are effective in promoting the removal of carbon monoxide in the presence of oxygen.

MONOLITH SYSTEM

With reference to FIGS. **8**, there is shown another embodiment of the present invention wherein a pair of monolith reactors **620**, **628** are arranged as swing reactors to desorb a stream such as the regenerator fluegas stream **619** which includes SOx and CO because any hydrogen sulfide fed to the regenerator **202** (FIG. **6**) with the catalyst by the conduit **205** is completely converted to SOx in the regenerator **202**. The sulfur oxide and CO containing gas stream **208** from the regenerator **202** is optionally cooled in a heat exchanger **213** to within a range of from about 900° F. to about 1400° F., and is fed by the line **219** to the top of the first monolith reactor **620** in the system. Each one of the monoliths **620**, **628** is formed of solid absorbent with unobstructed longitudinal passages provided by honeycomb structures **660**.

The solid absorbent monolith reactor **622** absorbs substantially all of the sulfur oxide from the sulfur oxide enriched gas stream **619** and converts the CO to CO_2 to provide a SOx and CO depleted gas stream through outlet conduit **624**. The SOx and CO depleted stream is fed through a valve system (not shown) to a line **625** leading to an incinerator or to a stack.

While in an absorbent mode, each monolith reactor **620**, **628** is operated at a temperature from about 900° F. to about 1,400° F. A temperature of from about 1,100° F. to about 1,300° F. is preferred. The oxygen content of the stream **219** entering the absorbent bed **222** is in an amount of from about 0.10 to about 10 vol %, 2 to about 4 vol % is preferred. Pressure within the reactor **200** should be maintained at a pressure of from about 0.1 to about 10 atmospheres, preferably from about 1.5 to about 3.0 atmospheres. GHSV should be from about 500 to about 20,000, and preferably from about 3,000 to about 5,000 GHSV. Operating the reactor **620** during the absorbent mode within these parameters converts substantially all carbon monoxide therein into carbon dioxide which is released into the environment. Other gases released from the reactor **620** include nitrogen, oxygen, and trace amounts of sulfur dioxide along with water.

The invention also contemplates that a fluegas stream from the overhead of the FCC regenerator **202** can be optionally fed through a furance (not shown) to insure that the stream feed is within the foregoing temperature ranges.

The outlet conduit **624** of the first monolith **620** is monitored by a sensor **626** until sulfur dioxide break-through occurs. A suitable sensor is a Siemens Ultramat 22P infrared analyzer. Of course, as will be understood by those skilled in the art, other comparable analyzing equipment can be used.

Sulfur dioxide break-through occurs when a substantial increase in the concentration of sulfur dioxide occurs in the conduit **624**. This increase will be in the order of from about 3 ppm to about 250 ppm.

When sulfur dioxide break-through is detected, the SOx and CO containing gas stream **619** is directed through a suitable valve system (not shown) into the top of the second monolith reactor **628**. Concurrently, the valve system directs a hydrogen rich stream **632** to the first reactor **620** for regeneration. The hydrogen rich stream **632** may contain hydrogen and/or hydrocarbons and/or syngas.

During regeneration of the monolith reactor **620**, the temperature is maintained between about 900° F. to about 1,400° F.; and the pressure in the reactor **620** is maintained at about 0.10 to about 10 atmospheres, preferably about 0.5 to about 3 atmospheres. The H_2 and/or hydrocarbon and or syngas stream **632** is directed into the reactor **620** at a gas hourly space velocity (GHSV) of about 10 to about 1,000, preferably about 100 to about 150. Initially, a GHSV of about 300 is preferred when commencing regeneration of a fixed-bed absorbent so that a higher concentration of liberated gases can be removed from the regenerator. As regeneration proceeds, the GHSV can be reduced to about 50 as the concentration of liberated gases diminishes.

Similarly, although hydrogen is the preferred reducing gas for regeneration, other hydrocarbon reducing gases can be used. These will preferably comprise C_1 through C_5 hydrocarbons. Substantially improved regeneration results are anticipated when water is co-fed into the reactor along with the hydrocarbons. The hydrogen and/or hydrocarbon and/or syngas stream **632** may contain 0.0 to 50% water. Also, syngas typically contains at least 10% hydrogen and at least 10% CO.

Regeneration of the reactor **620** provides a hydrogen sulfide and/or sulfur dioxide bearing stream through the outlet conduit **624**, the valve system (not shown), and via line **634** to the sulfur plant for recovery of sulfur. The hydrogen sulfide and/or sulfur dioxide bearing stream may also contain water and unconverted reducing gas.

The sulfur oxide and CO containing stream **619** and the hydrogen and/or hydrocarbon and/or syngas bearing stream **632** are alternately fed to each one of the reactors **620**, **628**, whereby each unit is first spent by sulfur oxides extracted from the stream **619**, and then regenerated by the hydrogen and/or hydrocarbon and/or syngas bearing stream **632**.

Compared to a conventional packed bed of solids, monoliths offer even lower pressure drop and less tendency to plug from the fine particles present particularly in FCC and coal combustion flue gas. Thus, this invention is particularly suitable for processing flue gas from FCC regenerators and from power plants. As discussed hereinafter, SOx sorbents can form the channeled monolith, or be formed as part of the channel monoliths, or be coated onto suitable monolithic supports.

Plugging is generally caused by fines typically catalyst fines, which accumulated in an extrudate bed and eventually plug up flow. However, with a channeled monolith, particularly in a straight downflow, the fines tend to get carried straight through. Even in a horizontal flow mode, the fines will tend to lay along the bottom of the channels and will eventually be carried along and therefore would very unlikely plug the channels. Therefore, it is preferable that the flow through the monolith be downward or that the monolith be on its side when fines are a factor. However, an embodiment wherein a fine laden stream is processed upwardly would be functional.

The monolith suitably has from about 25 cell/in^2 to about 800 cell/in^2 as viewed from an end thereof, and preferably from about 50 cell/in^2 to about 400 cell/in^2. A commercial size monolith may be in the order of a **16** foot long cylinder having about an 8 foot diameter. When the monolith is formed of extruded absorbent, it is preferred that the raw absorbent have a surface area at least about 130 m^2/g and that each extruded honeycombed structure have a surface area at least about 90 m^2/g to 130 m^2/g, and more preferably at least 130 m^2/g. Also, each one of the honeycombed structures can be extruded and then a plurality of the structures can be joined together to form the structure. Although it is preferred that the monolith have a circular cross-section, any cross-sectional is contemplated by this invention.

One conventional ceramic monolithic catalyst structure suitable for this invention consists of a ceramic support with a coating of high surface material on which the catalyst is deposited. Specifically, the ceramic support is prepared by first sintering a mold of clay or other ceramic material at a high temperature to impart density and strength. This procedure results in the ceramic having a very small surface area, and consequently the ceramic is coated with another material having a higher surface area, as well as specific chemical characteristics, on which to actually deposit the catalyst. This procedure of depositing a high surface area coat on the low surface area ceramic wall is disclosed, for example, in U.S. Pat. Nos. 2,742,437 and 3,824,196.

It is also known from U.S. Pat. No. 4,631,268 to make monolithic catalyst structure by initially forming separate moldable bodies of the materials for each of two phases that will form the monolithic support. Specifically, a moldable composition of a high surface arm oxide and plasticizing/binding agent for an oxide, as the support phase, is prepared separately from a second moldable composition of a sinterable ceramic material and a plasticizing/binding agent for the ceramic, as the matrix phase. Each composition is formed into shapes which are then intermingled for subsequent extrusion though a die to form the monolithic supports.

Porous oxides suitable for use as the support phase material are those which, after calcining, have a surface area of at least 20 square meters per gram, preferably at least 60 square meters per gram, and most preferably at least 100 square meters per gram. Preferably, the oxide is alumina, silica, a spinel, titania, zirconia or a zeolite. Mixtures of the oxides can also be used. Other materials which are commonly used as catalyst supports and which have the above-described characteristics can also be used.

Aluminas useful in the preparation of the high surface area support phase of this monolith are those which, upon calcining, provide gamma-alumina or other transition aluminas having the needed surface area. Colloidal gamma-alumina can be used directly, or "alumina-precursors" such as alpha-alumina monohydrate, or aluminum chlorohydrate can also be used.

Spinels useful in this monolith system are the magnesium aluminate spinels used as catalyst supports, including spinal solid solutions in which magnesium is partially replaced by such other metals as manganese, cobalt, zirconium, or zinc.

High surface area silica that can be used in preparing the high surface area composition for the support phase are the amorphous silicas of about **1-10** microns or sub-micron particle size. Readily-available zeolites useful to prepare the high surface area composition include the crystalline aluminosilicate zeolites designated A, X, and Y, and silicalite.

The ceramic material which is the basis for the matrix phase of the monolith can be any of the well known sinterable materials capable of providing mechanical strength and good thermal properties in the monolithic supports. The ceramic is suitably selected from cordierte, mullite, talc, clay, zirconia, zirconia-spinal, lithium aluminosilicates, alumina, silica and alumina-zirconia composites.

To construct the monolith of U.S. Pat. No. 4,631,268, the plasticized masses of high surface area support material and those of ceramic matrix material may be separately molded or formed into discrete bodies and then intermingled for coextrusion through a die to form the final desired shape of the monolithic catalyst support. This method is particularly suited to making honeycomb supports. The support and matrix bodies are typically intermingled to form a composite body in which the support bodies constitute a distinct, preferably discontinuous, phase throughout. The support bodies should also be at least substantially uniformly distributed throughout the composite. A proper distribution will be provided by a ratio of matrix bodies to support bodies of at least about 1.3:1 preferably at least 1.5:1. The size and shape of the matrix bodies and support bodies may be about the same. Using these ratios, the monoliths formed from such a composite will contain about 10–40 percent by weight of the high surface phase.

In one embodiment, the plasticized masses of high surface area material and those of ceramic material are separately extruded though a die into elongated shapes, of rectangular, hexagonal or circular cross-section.

The extruded bodies are then assembled into a single composite body by intermingling the rods axially or longitudinally. This may be done so that the rods are positioned with at least a substantially uniform distribution. Also the ratio of matrix bodies to support bodies is at least 1.5:1. After firing, monoliths formed from such a composite will contain about 10–40 percent by weight of the high surface phase.

The monolith shapes are heated to a temperature and for a time sufficient to sinter the ceramic material. Optionally, this heating/sintering step is preceded by drying the shapes at about 100°–120° C. The heating/sintering step generally takes place at 800°–1200° C. although when silicone resin is used as a binder for the ceramic matrix, particularly when the ceramic has a high alumina content, temperatures as low as 500° C. may be sufficient. Preferably, the temperature of the sintering step does not exceed about 1100°–1150° C. Despite the temperatures used to sinter the ceramic, the embedded porous oxide support phase retains high surface area and preferably provides the monolithic support with an overall surface area of at least 8–10 m^2/g, more preferably at least 15–20 m^2/g.

The monolithic supports may have some catalytic activity of their own because of the chemistry and structure of the high surface area phase. The support may further carry additional catalytically active ingredients dispersed throughout, but generally more concentrated at the high surface area sites provided by the embedded porous oxide support phase. Additional catalytic ingredients can be incorporated into the monolith by depositing them onto the support bodies after fabricating and sintering the final structure. U.S. Pat. Nos. 2,742,437, 3,824,196 and 4,631,268 are hereby incorporated herein by reference.

Also, in an embodiment to be described with reference to the following Example 6, the honeycombed structures are formed of absorbent.

EXAMPLE 6

Two monoliths were made of pure solid absorbent, each was 2 inch long and one inch in diameter. The solid absorbent was spray-dried Mg-Al spinel-based FCC additive sold by W. R. Grace Company under the trade name DESOX. After first grinding to powder and wetting of the absorbent, the monoliths were formed by extrusion.

One monolith has 200 cell/in^2 viewed from either end, and the other is a 400 cell/in^2 size. The 400 cell/in^2 unit has smaller openings and thinner walls, giving better mass transfer and diffusion characteristics, so more of the intrinsic or ultimate SOx uptake capacity (~60 wt. % SO_3/sorbent) of the absorbent is utilized before SOx breaks through at the exit end of the monolith. However, the 400 cell/in monolith has a higher pressure drop.

The test conditions were: 1200° F.; start with fresh or regenerated monolith (note: cycle-to cycle performance was stable, for the 5–10 cycles tested here); feed=1% SO_2, 4% O_2 (dry basis) with balance N_2; and about 10% water content was added via a bubbler. Regeneration between cycles was also at 1200° F. using H_2. Run until SO_2 breakthrough at 5 ppm was detected. The % uptake was calculated as grams of SO_3 taken up per grams of monolith times 100.

TABLE II

MONOLITH		UPTAKE (wt %)	
(cells/in^2)	FLOW RATE (cc/min)	5 ppm*	300 ppm*
200	830	19.2	25.7
	1660	9.6	16.1
400	830	48.7	53.0
	1660	40.1	47.5

*@breakthrough

Measured uptakes increase with lower flow rate and smaller cell sizes, due to lower ratios of (a) desired SOx mass transfer (from the gas phase to the solid surface, and from the solid surface to the interior of the solid cell wall) to (b) convection through the monolith to the exit, where breakthrough is detected. Uptakes naturally are higher when "breakthrough" is defined as 300 ppm, rather than 5 ppm SO2 detected at the exit. GHSV at standard conditions (~60° F., 1 atm) was about 1900 hr-1 for 830 cc/min, 3800 for 1660 cc/min.)

U.S. Pat. No. 5,229,091 for Process for Desulfurizing Claus Tail-Gas is incorporated herein by reference. U.S. Pat. No. 5,229,091 relates to a process for extracting sulfur from a gas containing hydrogen sulfide and sulfur oxide.

While the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modification, and variations as fall within the spirit and broad scope of the appended claims.

What is claimed is:

1. A method of removing nitrogen oxide, sulfur oxide and carbon monoxide from a combustion flue gas stream from a fluid catalytic cracking unit comprising a FCC reactor for converting a stream of petroleum feedstock in the presence of a fluidized bed of cracking catalyst into a stream of cracked product, a FCC regenerator for combusting coke buildup and other products from spent catalyst to thereby regenerate the spent catalyst and provide the combustion flue gas stream, a conduit for feeding spent catalyst from the FCC reactor to the FCC regenerator, and another conduit for passing regenerated catalyst from the FCC regenerator to the FCC reactor comprising the steps of:

combusting said coke buildup deposited on the spent catalyst in said FCC regenerator with a reduced amount of oxygen-containing gas ranging from about 95% to about 110% of the stoichiometric amount required to convert carbon monoxide into carbon dioxide to partially convert carbon monoxide therein to carbon dioxide and sufficient to convert all sulfur-containing species therein to sulfur oxide, and thus forming a sulfur oxide containing flue gas stream having at least 500 ppm carbon monoxide and the amount of nitrogen oxide in the sulfur oxide containing gas is an inverse function of the amount of carbon monoxide therein when the amount of oxygen containing gas fed to the combustor is reduced relative to the amount of oxygen containing gas needed to oxide all the carbon monoxide into carbon dioxide;

contacting said sulfur oxide containing flue gas stream and sufficient additional air with a solid adsorbent bed for adsorbing thereon the sulfur oxides in the form of inorganic sulfates or sulfur oxides or combinations thereof, the solid adsorbent containing a catalytic oxidation promoter for oxidizing the carbon monoxide in said sulfur oxide containing gas stream to carbon dioxide, and thus forming a sulfur oxide and carbon monoxide depleted stream for disposal; and

contacting said adsorbent bed with a reducing gas stream for regenerating said adsorbent bed by reducing said retained inorganic sulfates or sulfur oxides or combinations thereof to hydrogen sulfide and/or sulfur dioxide, and thereby forming a hydrogen sulfide and/or sulfur dioxide bearing stream.

2. The method of claim **1** wherein said solid adsorbent bed is a fluidized adsorbent bed in a fluidized adsorbent bed system comprising an adsorbent reactor, an adsorbent regenerator, a line for feeding spent adsorbent from the reactor to the adsorbent regenerator, and another line for passing regenerated adsorbent from the adsorbent regenerator to the adsorbent reactor; and wherein said sulfur oxide containing gas stream is fed to the adsorbent reactor to absorb said inorganic sulfates or sulfur dioxides or combinations thereof on the fluidized adsorbent therein, and said reducing gas stream is fed to the adsorbent regenerator to reduce said inorganic sulfates or sulfur oxides or combinations thereof on the fluidized adsorbent therein to form said hydrogen sulfide and/or sulfur dioxide bearing stream.

3. The method of claim **1** wherein said sulfur oxide containing flue gas stream includes at least one vol % of ppm carbon monoxide.

4. The method of claim **1** wherein less than 50% of carbon monoxide is converted in the adsorbent regenerator.

5. The method of claim **1** wherein said sulfur oxide containing flue gas stream contacting said solid adsorbent bed has an oxygen content of from about 0.1 vol % to about 10.0 vol %.

6. The method of claim **5** wherein oxygen content is from about 2 vol % to about 4 vol %.

7. The method of claim **1** wherein the solid adsorbent bed while absorbing the sulfur oxides thereon is operated at a gas hourly space velocity of from about 500 GHSV to about 20,000 GHSV, a pressure of from about 0.1 atmospheres to about 10.0 atmospheres, and a temperature of from about 900° F. to about 1400° F.

8. The method of claim **7** wherein the GHSV is from about 3,000 to about 5,000.

9. The method of claim **7** wherein said temperature is from about 1,100° F. to about 1,300° F.

10. The method of claim **7** wherein said pressure is from about 1.5 atmospheres to about 3.0 atmospheres.

11. The method of claim **1** wherein the solid adsorbent bed while being regenerated is operated at a temperature of from about 900° F. to about 1,400° F., at a pressure of from about 0.10 atmospheres to about 10.0 atmospheres, and a gas hourly space velocity 10 GHSV to about 1,000 GHSV.

12. The method of claim **11** wherein said temperature is from about 1,100° F. to about 1,300° F.

13. The method of claim **11** wherein said pressure is from about 0.5 atmospheres to about 3.0 atmospheres.

14. The method of claim **11** wherein said GHSV is from about 100 to about 150.

15. The method of claim **1** wherein the solid adsorbent is alumina impregnated with a rare earth.

16. The method of claim **1** wherein the solid adsorbent is Mg/Al spinels.

17. The method of claim **1** wherein the solid adsorbent is magnesium, aluminum-containing spinel impregnated with vanadium and cerium.

18. The method of claim **1** wherein the solid adsorbent is magnesium aluminate, and wherein the catalytic oxygen promoter is impregnated in said magnesium aluminate.

19. The method of claim **18** wherein said promoter is CeO_2 and/or Pt.

20. The method of claim **1** wherein the solid adsorbent bed comprises a plurality of longitudinally extending honeycombed structures, the honeycombed structures having solid absorbent on the inner surfaces thereof or being formed at least in part of solid absorbent, the sulfur oxide enriched gas stream and the reducing gas stream being alternately passed from the inlet end to the outlet end of said honeycombed structures.

21. The method of claim **20** wherein the solid adsorbent is alumina impregnated with a rare earth.

22. The method of claim **20** wherein the solid adsorbent is Mg/Al spinels.

23. The method of claim **20** wherein the solid adsorbent is magnesium, aluminum-containing spinel impregnated with vanadium and cerium.

24. The method of claim **20** wherein the solid adsorbent is magnesium aluminate impregnated with an oxygen promoter.

25. The method of claim **20** wherein said promoter is CeO_2 and/or Pt.

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UNITED STATES PATENT AND TRADEMARK OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 5,547,648

DATED : August 20, 1996

INVENTOR(S) : John S. Buchanan et al.

It is certified that error appears in the above-indentified patent and that said Letters Patent is hereby corrected as shown below:

Col. 25, line 18, Claim 1, delete "a reduced" and insert --an--.

Signed and Sealed this

Twenty-ninth Day of October 1996

Attest:

Bruce Lehman

BRUCE LEHMAN

Attesting Officer

Commissioner of Patents and Trademarks